JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC CHEMISTRY.

1904. Vol. LXXXVI. Part I.

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW.
1904.

Richard Clay & Sons, Limited,
BREAD STREET HILL, E.C., AND
BUNGAY, SUFFOLK.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Asymmetric Carbon Atom. ERNST MOHR (*J. pr. Chem.*, 1903, [ii], **68**, 369—384. Compare Rabe, Abstr., 1901, i, 33; Aschan, Abstr., 1903, ii, 2).—A theoretical paper. G. Y.

Action of Fuming Sulphuric Acid on *iso*Amyl Chloride. ROBERT A. WORSTALL (*J. Amer. Chem. Soc.*, 1903, **25**, 932—935).—*iso*Amyl chloride was sulphonated by fuming sulphuric acid, and acicular crystals of the barium salt, $(OH \cdot C_5H_{10} \cdot SO_3)_2Ba,2H_2O$, were isolated. A concentrated aqueous solution of the salt, when boiled with dilute hydrochloric acid, did not develop a pink colour; no precipitate formed, and no odour of fusel oil was perceptible. The free acid, obtained from the lead salt by hydrogen sulphide, contained only a trace of sulphuric acid after being boiled with water. *iso*Amyl sulphate is possibly the initial product of the sulphonation, and, by further action, is converted into the hydroxysulphonic acid.

A. McK.

Action of Water on Methylene Dibromide. KARL KLÖSS (*Monatsh.*, 1903, **24**, 783—789. Compare Jeltekow, *Ber.*, 1873, **6**, 558).—When heated with water at 150°, methylene dibromide is hydrolysed with formation of formaldehyde. After heating for 30 hours, the yield of formaldehyde is 89·1 per cent. of the theoretical; a 93·8 per cent. yield of formaldehyde is obtained on heating methylene dibromide with lead oxide and water for 26 hours at 150°. The author discusses the methods of estimating formaldehyde (see Legler, Abstr., 1883, 1035; Lösekann, Abstr., 1889, 1036; Eschweiler Abstr., 1889, 1250; Blank and Finkenbeiner, Abstr., 1899, ii, 188 820). G. Y.

Nitromethane as a Solvent. LUDWIK BRUNER (*Ber.*, 1903, **36**, 3297—3298).—[With J. KOZAK and G. MARIASZ.]—Pure nitromethane has a specific conductivity $k = 6 \cdot 4 \times 10^{-7}$ inverse ohms at 18°. Very few electrolytes are soluble in nitromethane, but measurements are given for the molecular conductivity of tribromoacetic acid, antimony trichloride and tribromide, and mercury chloride in this solvent which show that it possesses ionising power, although the magnitude of this is very much less than might be anticipated from its high dielectric constant.

Chloropicrin has a specific conductivity $6 \cdot 0 \times 10^{-8}$ inverse ohms, and is less ionising than nitromethane. W. A. D.

Hydrates of Ethyl Alcohol. EUGÈNE VARENNE and L. GODEFROY (*Compt. rend.*, 1903, **137**, 993—996).—Solutions of ethyl alcohol in water have been examined by means of a special form of constant pressure capillary viscosimeter. The curve representing the viscosity shows a principal maximum corresponding with the well-known hydrate $C_2H_6O,3H_2O$, and also indicates the existence of hydrates with $2H_2O$ and $6H_2O$, and also, less distinctly, $3C_2H_6O,2H_2O$ and $C_2H_6O,22H_2O$. C. H. D.

Action of Organo-magnesium Compounds on Acetol and its Esters. ANDRÉ KLING (*Compt. rend.*, 1903, **137**, 756—758).—The author has examined the behaviour of acetol and its esters with organo-magnesium compounds at low temperatures in order to determine whether they contain the $-CO-$ or $:\underbrace{C-C}_{O}:$ group (Abstr., 1903, i, 138), since, under these conditions, compounds containing the former grouping yield a tertiary alcohol of the type $CRR'R'' \cdot OH$ (Grignard, Abstr., 1900, i, 382), whilst compounds containing the latter grouping give secondary alcohols of the type $OH \cdot CHR \cdot CH_2X$, where X is a halogen radicle (Grignard, Abstr., 1903, i, 552). Acetol and its esters behave like ketonic compounds, yielding glycols, thus the *amylene glycol*, $OH \cdot CMeEt \cdot CH_2 \cdot OH$, was obtained from magnesium ethiodide and acetol acetate; *methyldiethylcarbinol*, $CMeEt_2 \cdot OH$, and *amylene glycol* from magnesium ethobromide and acetol acetate; magnesium methiodide and acetol acetate yielded the monoacetyl derivative of *butyl glycol*, $OH \cdot CMe_2 \cdot CH_2 \cdot OH$, whilst acetol benzoate yielded *phenyldiethyl carbinol*, $CPhEt_2 \cdot OH$, magnesium benzoate, and *amylene glycol*. M. A. W.

Conversion of the αγ-Glycol from *iso*Butaldehyde into the Isomeric αδ-Glycol. GUSTAV MOSSLER (*Monatsh.*, 1903, **24**, 595—617. Compare Fossek, Abstr., 1884, 37, 832; Swoboda and Fossek, Abstr., 1891, 31; Franke, Abstr., 1896, i, 404).—The action of hydrobromic acid of sp. gr. 1·75 on Fossek's glycol and on the two oxides obtained by boiling the glycol with dilute sulphuric acid leads to the formation of αδ-dibromo-ββδ-trimethylpentane. The reaction takes place most easily with the more volatile oxide; with the glycol, a small amount of the less volatile oxide is formed. In each case, there is obtained a liquid bromo-derivative which boils at 58—60° under 14—16 mm.

pressure. *αδ-Dibromo-ββδ-trimethylpentane*, $CH_2Br·CMe_2·CH_2·CMe_2Br$, crystallises from light petroleum in colourless, almost odourless, rhombic plates and prisms, melts at 68°, and boils at 102—103° under 14 mm. pressure. When boiled with water, with dilute aqueous potassium carbonate solution, or with moist silver oxide (1 mol.) and water, the dibromide yields the oxide boiling at 120—122°. With an excess of silver oxide, the dibromide yields *ββδ-trimethylamylene-αδ-glycol*, $OH·CH_2·CMe_2·CH_2·CMe_2·OH$, which separates from ether in clusters of feathery crystals, melts at 86°, boils at 114—115° under 13 mm., at 209—211° under atmospheric pressure, and is isomeric with Fossek's glycol. The *diacetate*, formed by the action of silver acetate on the dibromide, is a colourless liquid, boils at 111—112° under 11 mm., at 214—216° under the ordinary pressure, and is hydrolysed to the glycol when boiled with 40 per cent. alcoholic potassium hydroxide.

The αδ-glycol is not acted on by neutral potassium permanganate solution at the laboratory temperature, but on warming it is completely decomposed. Alkaline potassium permanganate solution oxidises the glycol to a liquid substance which distils at 80—150° under the ordinary pressure. Acid oxidising agents decompose the glycol.

When boiled with dilute sulphuric acid in a reflux apparatus or when heated with water at 180°, the αδ-glycol yields the more volatile oxide.

As suggested by Franke, the oxide boiling at 120—122° must be represented by the constitutional formula $\begin{matrix} CH_2·CMe_2 \\ | \\ CMe_2·CH_2 \end{matrix}\!\!>\!O$, the oxide boiling at 260—262° by the formula $(C_8H_{16})_2O_2$. G. Y.

Formation of Normal Diprimary Decylene Glycol (Decan-ακ-diol) by Reduction of Derivatives of Sebacic Acid. RUDOLF SCHEUBLE (*Monatsh.*, 1903, 24, 618—632).—Reduction of sebacamide with sodium and amyl alcohol leads to the formation of decamethylene ακ-glycol and a small amount of decamethylene-ακ-diamine.

Decamethylene ακ-glycol, $OH·CH_2[CH_2]_8·CH_2·OH$, crystallises in long, white needles, melts at 70°, boils at 179° under 15 mm., or at 192° under 20 mm. pressure, and is soluble in ether, chloroform, or benzene, but less so in water or light petroleum. The *diacetate*, $C_{10}H_{20}(OAc)_2$, is a colourless, crystalline mass, which melts at 25·5°, boils at 170·5° under 10 mm. pressure, and is easily soluble in organic solvents.

The glycol is oxidised to sebacic acid by potassium permanganate in neutral solution. G. Y.

Action of Chlorine on Barium Acetate. ALBERT COLSON (*Compt. rend.*, 1903, 137, 660—661).—When chlorine is passed into a solution of barium acetate in an acetic acid solution containing acetic anhydride at 12°, it forms a double salt, barium acetochloride, crystallising with one molecular proportion of acetic acid,

$$BaCl·OAc,C_2H_4O_2,$$

insoluble in acetic acid, but soluble in water. Curie has examined the barium precipitated from this compound with respect to

its radioactive properties, and finds that if it acquires radioactivity at all it is less than 1/20 that of uranium. M. A. W.

Hydrolysis and Synthesis of Fats by Platinum Black. HUGH NEILSON (*Amer. J. Physiol.*, 1903, 10, 191—200).—Platinum black accelerates the hydrolysis of ethyl butyrate as lipase does, only its action is slower. Its action, like that of lipase, increases with the increased concentration of the platinum, and is independent of the concentration of the ethyl butyrate. The action increases with temperature, reaching its maximum at 50°. Various poisons (thymol, salicylic acid, chloroform, phenol, &c.) affect the catalytic action of platinum as they do that of lipase. Sodium fluoride and hydrocyanic acid, however, have no effect. Platinum black also synthesises butyric acid and ethyl alcohol into ethyl butyrate; this is comparable to the "reversible" action of lipase. W. D. H.

Fats. ALFRED PARTHEIL and F. FERIÉ (*Arch. Pharm.*, 1903, 241, 545—569).—In the separation of fatty acids by means of the solubility or insolubility of their lead salts in benzene (Farnsteiner, *Zeit. Nahr. Chem.*, 1898, 390), the results are sometimes vitiated by the formation of a mixed lead salt, such as lead oleo-stearate. Obviously this might be avoided by using, not lead salts, but salts of a univalent metal; on this account, the solubility of the lithium salts of various fatty acids in water and alcohol of sp. gr. 0·797 was determined, in order to ascertain whether they could be utilised for the purpose. The acids employed were obtained by purifying the commercial specimens; they had the following constants:

Acid.	M. p.	B. p.	n_D.
Stearic	70·5°	238° under 17 mm.	1·4325 at 71°
Palmitic	62·5	219 ,, 17 ,,	1·4284 ,, 74·5
Myristic	53·7	199 ,, 16 ,,	1·4248 ,, 76·5
Lauric	43	177 ,, 16 ,,	1·4236 ,, 76
Oleic	—	241 ,, 20 ,,	— —

The salts were usually prepared by heating the alcoholic solution of the acid with a slight excess of lithium carbonate, and allowing the filtered solution to cool. The oleate, however, was prepared by mixing aqueous solutions of potassium oleate and lithium acetate, and crystallising the precipitate from alcohol. For the determination of the solubility, the salts were shaken for 48 hours with 200 c.c. of the solvent in bottles of Jena glass in a thermostat; the lithium salt was then estimated in aliquot parts of the filtrate. The results are tabulated below, the numbers indicating grams of the salt in 100 c.c. of the saturated solution.

Lithium salt.		Water. 18°	Water. 25°	Alcohol. 18°	Alcohol. 25°
Stearate,	$C_{17}H_{35}\cdot CO_2Li$	0·010	0·011	0·041	0·053
Palmitate,	$C_{15}H_{31}\cdot CO_2Li$	0·011	0·018	0·080	0·096
Myristate,	$C_{13}H_{27}\cdot CO_2Li$	0·023	0·023	0·184	0·210
Laurate,	$C_{11}H_{23}\cdot CO_2Li$	0·158	0·173	0·418	0·442
Oleate,	$C_{17}H_{33}\cdot CO_2Li$	0·067	0·132	0·908	1·009

Partly as a result of these determinations, the following method of

analysis was elaborated. About 1 gram of the fat is saponified with 15 c.c. of approximately $N/2$ alcoholic potassium hydroxide on the water-bath, the soap dissolved in 100 c.c. of 50 per cent. alcohol, and the solution neutralised with dilute acetic acid, phenolphthalein serving as the indicator. The lithium salts of the higher fatty acids are precipitated by adding a 10 per cent. solution of lithium acetate in 50 per cent. alcohol, the precipitate redissolved by warming to about 60°, and the solution allowed to cool, when lithium stearate, palmitate, and most of the myristate crystallise out. The crystals are filtered off, washed with 50 per cent. alcohol, dried, weighed roughly, dissolved in hot absolute alcohol, and the solution allowed to cool. The stearate and palmitate crystallise out, and are collected, dried at 100°, and weighed. The solution of myristate is evaporated, and the residue dried at 100° and weighed. Each residue is then decomposed with hydrochloric acid, and the liberated acid washed, dried, and titrated with alkali; thus in the one case the proportion between the stearic and palmitic acids is determined, in the other the myristic acid is identified.

The lithium salts that remain dissolved are converted into the lead salts, and these extracted with hot benzene. The insoluble residue is decomposed with hydrochloric acid and the proportion between the myristic and lauric acids determined by titration with alkali. The benzene solution is evaporated in a current of hydrogen, the residue decomposed with dilute hydrochloric acid, the liberated acids dissolved in alcohol, neutralised with potassium hydroxide, and converted into barium salts by means of 10 per cent. barium acetate solution. By extraction with ether saturated with water, the barium salts of the acids of the linoleic acid series are dissolved, and their weight, as well as that of the residual barium oleate, is determined.

In this way, the results tabulated below were obtained. The lard was of American origin. Of human fat, 7 samples were examined so far as regards the determination of the usual constants; these came from different parts of the body, and from both men and women. Two samples, one from a man, the other from a woman, were further analysed. Distinct amounts of acids of the linoleic series were found in human fat, in margarine, in lard, and also in butter. From the human fat, a liquid mixed glyceride, *dioleostearin*, was isolated.

	Butter.		Margarine.	Lard.	Human Fat.	
Iodine number	35·2	36·4	69·5	65·8	57—66	
Reichert-Meissl number	33·1	28·6	—	—	1·1—2·1	
Köttstorfer number	—	—	—	—	194—198	
Hehner number	—	—	—	—	94—96	
Stearic acid	6·6	10·5	19·1	8·4	12·3	12·4
Palmitic acid	18·2	14·5	6·1	4·5	29·2	27·0
Myristic acid	11·1	11·9	14·3	14·4	—	—
Lauric acid	16·4	14·9	7·0	11·7	—	—
Unsaturated acids *	30·7	32·6	47·1	54·0	48·6	53·0
	83·0	84·4	93·6	93·0	90·1	92·4
* Of linoleic series	5·4	4·1	20·3	10·0	—	—
Iodine number (of unsaturated acids)	115	112	148	122	—	—

C. F. B.

Theory of the Saponification Process. Julius Lewkowitsch (*Ber.*, 1903, 36, 3766—3768).—A reply to the criticisms of Balbiano (Abstr., 1903, i, 547). T. M. L.

Behenolic Acid. M. Haase and Albert Stutzer (*Ber.*, 1903, 36, 3601—3604).—*Behenolic chloride*, $C_{22}H_{39}OCl$, crystallises in needles and melts at 29—30°; it cannot be distilled in a vacuum without decomposition. The *ethyl* ester, $C_{24}H_{44}O_2$, forms minute, white needles, and melts at 15—16°. The *phenyl* ester, $C_{28}H_{44}O_2$, forms glistening, white, fatty scales and melts at 43°. The *anilide*, $C_{28}H_{45}ON$, forms monoclinic prisms and melts at 72°. The *acetanilide*, $C_{30}H_{47}O_2N$, crystallises from ethyl acetate in minute, white needles and melts at 45°. The *amide* forms glistening, fatty scales, melts at 90°, and, like behenolic acid, becomes pyroelectric when rubbed.

Monobromobrassidic acid is produced in good yield when an ethereal solution of behenolic acid is saturated with hydrogen bromide in the cold and then gently warmed; it is reduced by sodium to brassidic acid, $C_{22}H_{40}O_2$, melting at 59°, whilst bromine water converts it into *dibromohydroxybehenic acid*, $C_{22}H_{42}O_3Br_2$, a colourless oil, solidifying to a crystalline mass which melted at 46—47°. By the action of alcoholic sodium hydroxide, the latter acid is converted into a *brominated glycidic acid*, $C_{22}H_{41}O_3Br$, which forms minute, silky needles and melts at 44°; dilute acids and alkalis convert this into *bromodihydroxybehenic acid*, $C_{22}H_{43}O_4Br$, which forms glistening, white scales and melts at 71°. T. M. L.

Chloro- and Bromo-hydroxybehenic Acids and their Transformation Products. D. Warmbrunn and Albert Stutzer (*Ber.*, 1903, 36, 3604—3606).—Chloro- and bromo-hydroxybehenic acids are readily obtained in a pure state by the action of chlorine or bromine on the sodium salts of erucic or brassidic acids, sodium haloid being eliminated. The derivative from erucic acid is hydrolysed by sodium hydroxide, forming a glycidic acid, $C_{22}H_{42}O_3$, separating from ether as a fine, white powder melting at 64°, insoluble in water, but dissolving readily in organic solvents. Its salts are amorphous and dissolve in alcohol. Ammonia reacts with the sodium salt in alcoholic solution at 140° to form *aminohydroxybehenic acid*, $C_{22}H_{45}O_3N$, a white, amorphous powder melting at 86°, dissolving sparingly in alcohol, readily in glacial acetic acid. Acetic anhydride forms an *anhydride* of *diacetoxybehenic acid*, $C_{26}H_{48}O_6$, crystallising in small needles melting at 63°. Heating with potassium hydroxide solution at 170° further hydrolyses it to dihydroxybehenic acid melting at 99°, and identical with that obtained by Albitzky (Abstr., 1899, i, 862). The chloro-derivative from brassidic acid reacts in a similar manner, forming a glycidic acid separating from alcohol in crystals melting at 71° and dissolving in ether. Further hydrolysis gives rise to the dihydroxybehenic acid melting at 133°, which also results from the direct oxidation of erucic acid. C. H. D.

Oxidation of Oxalic Acid by Free and Combined Oxygen. Willem P. Jorissen and Lodewyk T. Reicher (*Zeit. Farb. Text.-Chem.*, 1903, 2, 431—435).—Mainly a review of previous work on the

subject. The oxidation of oxalic acid solutions by gaseous oxygen (compare Richardson, Trans., 1894, 65, 450; Jorissen, Abstr., 1899, 739; Jorissen and Reicher, Abstr., 1900, ii, 200), hydrogen peroxide, potassium permanganate, and chromic acid (Werner, Trans., 1887, 51, 388; Prudhomme, Abstr., 1903, ii, 430) is discussed. Werner's equation, $H_2Cr_2O_7 + 9H_2C_2O_4 = H_6Cr_2(C_2O_4)_6 + 7H_2O + 6CO_2$, involving the formation of chromoxalic acid in the oxidation of oxalic acid by chromic acid is confirmed by quantitative measurements. In presence of an excess of sulphuric acid and chromium sulphate, the oxidation in this case is a reaction of the first order. The remainder of the paper deals with the oxidation of oxalic acid solutions by chromic acid in presence of indigotin (compare von Georgievics, *Zeit. Farb. Text.-Chem.*, 1903, 2, 200). W. A. D.

Compounds of Quadrivalent Vanadium. II. IWAN KOPPEL and R. GOLDMANN (*Zeit. anorg. Chem.*, 1903, 36, 281—301. Compare Abstr., 1903, ii, 551).—*Ammonium divanadyl oxalate*,

$$(NH_4)_2C_2O_4,2VOC_2O_4,6H_2O,$$

prepared (1) by melting together oxalic acid and ammonium metavanadate and then extracting the mass with alcohol, or (2) by dissolving ammonium metavanadate (2 mols.) and oxalic acid (4 mols.) in water and then adding acetone, forms greenish-blue crystals and is easily soluble in water. *Ammonium vanadyl oxalate*,

$$(NH_4)_2C_2O_4,VOC_2O_4,2H_2O,$$

prepared from ammonium metavanadate (2 mols.), oxalic acid (4 mols.), and ammonium oxalate (1 mol.), is distinguished from the divanadyl oxalate by being more readily crystallisable and by its blue colour. *Potassium divanadyl oxalate*, $K_2C_2O_4,2VOC_2O_4,4H_2O$, is blue, and can be crystallised from water. *Sodium divanadyl oxalate*,

$$Na_2C_2O_4,2VOC_2O_4,8\tfrac{1}{2}H_2O,$$

separates in dark blue clusters of needles.

Ammonium vanadyl thiocyanate, $(NH_4)_2VO(CNS)_4,5H_2O$, prepared from an aqueous solution of its components by precipitation with ethyl acetate, forms rhombic crystals [$a:b:c = 0·991:1:0·607$]. *Potassium vanadyl thiocyanate*, $K_2VO(CNS)_4,5H_2O$, is isomorphous with the ammonium salt [$a:b:c = 0·9163:1:0·5469$]. The corresponding sodium salt could not be isolated.

A quantitative method of separating vanadium, based on the solubility of ammonium vanadyl thiocyanate in a mixture of 9 parts of ether and 1 part of amyl alcohol, is described.

Ammonium vanadite, $(NH_4)_2V_4O_9,xH_2O$, prepared by the addition of a boiling solution of a vanadyl salt to ammonia, separates in glistening brown needles or scales. Its aqueous solution is readily oxidised on exposure to the atmosphere. *Sodium vanadite*,

$$Na_2V_4O_9,4H_2O,$$

forms golden needles or scales. *Potassium vanadite*, $K_2V_4O_9,4H_2O$, and *barium vanadite*, $BaV_4O_9,4H_2O$, are described, but silver vanadite could not be prepared. A. McK.

Use of Magnesium Amalgam in Organic Chemistry. LOUIS MEUNIER (*Compt. rend.*, 1903, 137, 714—716. Compare Abstr., 1902, i, 335).—Diphenylmethane is conveniently prepared by the action of

magnesium amalgam on a mixture of benzyl chloride and bromobenzene. Ethyl malonate is not attacked by magnesium, even on warming, but when dissolved in benzene the reaction occurs readily, the magnesium entering the methylene group of the ester. The compound thus formed reacts with ethyl iodide, forming ethyl ethylmalonate, which may be converted into ethyl diethylmalonate by treatment with magnesium ethoxide and subsequent action of ethyl iodide. Magnesium ethyl iodide acts on the methylene group of ethylmalonate, hydrolysis of the ester taking place when an excess of the magnesium compound is used. C. H. D.

Action of Sulphur Chloride on Ethyl and Methyl Malonates. Heinrich Wolff and A. Ott (*Ber.*, 1903, 36, 3721—3726).—Ethyl malonate reacts with sulphur chloride in presence of aluminium chloride, forming a gelatinous mass of *ethyl dithiomalonate*, $S_2[CH(CO_2Et)_2]_2$, which separates from hot acetone as an almost colourless syrup, converted by repeated precipitation with water from alcoholic solution into rosettes of small needles melting at 131°, and very sparingly soluble in organic solvents with the exception of carbon disulphide. The syrupy form is more readily soluble in all solvents, but shows no difference in composition or molecular weight. Phenylhydrazine decomposes the sulphide with formation of sulphur and hydrogen sulphide.

Methyl malonate reacts with sulphur chloride in presence of aluminium chloride at 70—80°. The crystalline product is extracted with acetone and recrystallised from alcohol. *Methyl trithiomalonate*, $S_3[CH(CO_2Me)_2]_2$, forms white, flexible needles with green lustre, melting at 167° and dissolving readily in benzene, carbon disulphide, glacial acetic acid, or hot acetone, insoluble in water or ether. The mother-liquor deposits a further small quantity of the same substance after 3—4 weeks. The remainder of the syrup is repeatedly dissolved in alcohol and precipitated with water, and then yields a clear, viscous syrup, which deposits a small quantity of *methyl thiomalonate*, $S[CH(CO_2Me)_2]_2$, as white rhombohedra, melting at 122° and dissolving readily in ether, benzene, glacial acetic acid, or alcohol, less soluble in acetone; it may also be prepared by the action of sulphur dichloride on methyl malonate. Both the mono- and trithio-compounds react with phenylhydrazine, forming *thiomalonic hydrazide*, $C_{30}H_{30}O_4N_8S$, crystallising from 60 per cent. alcohol in glistening, white prisms melting at 120°. This reaction can only be explained by assuming the grouping :CH·S·CH: in the trithio-ester, the grouping :CH·S·S·S·CH:,

S S

suggested by Angeli and Magnani (Abstr., 1894, i, 547) being excluded. C. H. D.

Preparation of Adipic Acid. Louis Bouveault (*Bull. Soc. chim.*, 1903, [iii], 29, 1038—1043).—The author found that a solution of sodium methyl succinate, prepared by the addition of a solution of sodium methoxide in methyl alcohol to finely powdered succinic

anhydride suspended in methyl alcohol, when electrolysed, furnished 70 per cent. of the theoretical amount of methyl adipate. The apparatus employed consisted of a two litre flask, fitted with an india-rubber stopper carrying an iron wire in contact with a layer of mercury (constituting the negative electrode) in the flask. The positive electrode was a spiral tube of platinum, through which a rapid current of cold water circulated. The electrolyte had a resistance of four ohms, and a current of 7 to 8 amperes and 25 to 30 volts was necessary to effect the change. Sodium ethyl succinate dissolved in ethyl alcohol proved to be too highly resistant to permit of the preparation of ethyl adipate by this process, but aqueous solutions of the salt when electrolysed gave small yields of ethyl adipate.

Methyl adipate is a colourless liquid of unpleasant odour; it boils at 115° under 13 mm. pressure, crystallises when cooled to 0°, and melts at 8°.

α-Hydroxysuberic and $\alpha\theta$-dihydroxysebacic acids, prepared by Weger's process (Abstr., 1894, 359), can be separated readily from the by-products of the reaction by precipitation as the cupric salts and regeneration of the acids from these by the action of hydrogen sulphide on the salts suspended in water. T. A. H.

By-products of the Electrolytic Preparation of Adipic Acid. Louis Bouveault (*Bull. Soc. chim.*, 1903, [iii], 29, 1043—1046. Compare preceding abstract).—When sodium ethyl succinate is electrolysed in aqueous solution, carbon dioxide is evolved and the surface of the electrolyte becomes covered with an oily layer. When the reaction liquid is extracted with ether and the residue left after evaporating off the solvent is distilled under reduced pressure, four fractions are obtained. The first of these consists of ethyl propionate with a small quantity of ethyl acrylate (compare Brown and Walker, Abstr., 1891, 1192, 1193), the second of ethyl β-hydroxypropionate (Klimenko and Rufalowicz, *J. Russ. Phys. Chem. Soc.*, 1894, 26, 413), probably formed by the combination of ethyl acrylate (1 mol.) with water (1 mol.); the third is principally ethyl adipate, whilst the fourth is the *triethyl ester* of an acid having the formula $CO_2H\cdot CH_2\cdot CH(CH_2\cdot CH_2\cdot CO_2H)_2$ or

$$CO_2H\cdot CH(CH_2\cdot CH_2\cdot CO_2H)CH_2\cdot CH_2\cdot CH_2\cdot CO_2H.$$

It boils at 195—205° under 10 mm. pressure and has a sp. gr. 1·072 at 0°/4°. The free *acid* is very soluble in water and crystallises with difficulty.

The products of the electrolysis of sodium methyl succinate, dissolved in methyl alcohol, may be similarly separated into three fractions, the first consisting of methyl adipate, the second of *methyl hydrogen succinate*, which is crystalline, melts at 57—58°, boils at 151° under 20 mm. pressure, and is readily soluble in water and organic solvents. This ester is not produced during electrolysis, but is formed by the fractional distillation of the crude oil. The third portion is probably the *trimethyl ester* of the acid $C_9H_{14}O_6$, similarly obtained from sodium ethyl succinate. It is a colourless oil, boils at 194° under 20 mm. pressure, and has a sp. gr. 1·132 at 0°/4°. T. A. H.

Synthesis of β-Methyladipic Acid. William A. Noyes and Irving J. Cox (*J. Amer. Chem. Soc.*, 1903, 25, 1093—1096).—It has been shown by Noyes (Abstr., 1901, i, 631) that ethyl 1-cyano-2 : 2-dimethyl*cyclo*pentane-5-one-1-carboxylate is decomposed by sodium hydroxide with formation of the sodium salts of malonic and hydroxy-*iso*hexoic acids. In order to determine whether this reaction is of general application, an attempt has been made to prepare a similar compound containing only one methyl group.

By the condensation of ethyl γ-chlorovalerate with ethyl cyano-acetate in presence of sodium ethoxide, a small quantity of a crystalline substance was obtained which melts at 185° and is probably *ethyl 1-cyano-2-methyl*cyclo*pentane-5-one-1-carboxylate*,

$$\begin{matrix} CH_2\text{——}CO \\ CH_2\cdot CHMe \end{matrix}{>}C(CN)\cdot CO_2Et,$$

but the amount was insufficient for further examination.

Ethyl α-cyano-β-methyladipate,

$$CO_2Et\cdot CH(CN)\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

obtained by the condensation of ethyl bromovalerate with ethyl cyanoacetate, boils at 175—185° under 20 mm. pressure. When this ester is hydrolysed with alcoholic sodium hydroxide, *β-methyl-butane-ααδ-tricarboxylic acid* is produced, which crystallises in plates, melts and decomposes at 127—128°, and when heated at 200° is converted into β-methyladipic acid; its *calcium* salt crystallises with $3H_2O$.

Ethyl α-cyano-αβ-dimethyladipate,

$$CO_2Et\cdot CMe(CN)\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

prepared by the action of methyl iodide on ethyl cyanomethyladipate in presence of sodium ethoxide, boils at 181—194° under 29 mm. pressure, and, on hydrolysis, yields *αβ-dimethylbutane-ααδ-tricarboxylic acid*, which forms white, pearly crystals, melts at 159°, and if heated at 200° is converted into αβ-dimethyladipic acid. E. G.

Preparation of Ethyl Glutaconate. Edmond E. Blaise (*Bull. Soc. chim.*, 1903, [iii], 29, 1012—1015. Compare Abstr., 1903, i, 400 and 548).—Sodium acetonedicarboxylate, prepared by Jerdan's method (Trans., 1899, 75, 809), is reduced by sodium amalgam (von Pechmann and Jenisch, Abstr., 1891, 147) and the resulting β-hydroxyglutaric acid freed from associated β-hydroxybutyric acid by conversion into the ethyl ester and fractionation of this under reduced pressure.

When β-hydroxyglutaric acid is treated with acetyl chloride, it is converted into the anhydride of β-acetoxyglutaric acid; ethyl β-hydroxyglutarate, on the other hand, either by acetic anhydride or acetyl chloride is converted into ethyl β-acetoxyglutarate, which, when distilled under atmospheric pressure, is decomposed into acetic acid and ethyl glutaconate. The yields of ethyl β-hydroxyglutarate and ethyl glutaconate obtained by this process amounted to 43 and 30 per cent. respectively of the weight of acetonedicarboxylic acid used.

T. A. H.

Optical Rotatory Power of Glutamic Acid. Karl Andrlík (*Zeit. Ver. deut. Zuckerind.*, 1903, 572, 948—958).—The author has

studied the influence of foreign substances on the rotation of pure glutamic acid prepared from molasses residues and having $[\alpha]_D$ $+12{\cdot}04°$ in 1 per cent. solution at 20°. Weak acids such as boric, acetic, &c., are almost entirely without influence. Increasing amounts of strong acids cause a continuous increase of the specific rotation which tends towards a maximum. The addition of bases first changes the dextro- into a lævo-rotation, which attains its highest numerical value with the formation of the acid salt; further quantities of base convert the lævo- back into a dextro-rotation. With lead hydroxide, however, no change in sign of the rotation takes place. Basic lead acetate, in small quantities, diminishes the rotation, and in larger quantities changes it to a lævo-rotation which increases considerably as the amount of acetate is increased. Betaine, in small proportions (1·5 per cent.), has no effect on the rotation. T. H. P.

Oxalacetic Acid. Louis J. Simon (*Compt. rend.*, 1903, **137**, 855—857).—The author shows that it is possible to obtain oxalacetic acid from the ester by hydrolysis. The freshly distilled ester (one part) is mixed with concentrated hydrochloric acid (four parts) and shaken to assist solution. After the lapse of forty-eight hours at the ordinary temperature, the reaction is complete. Oxalacetic acid obtained by this method is identical with that prepared in other ways. It can be distinguished from a mixture of acetic and oxalic acids by the following reactions: aqueous or alcoholic ferric chloride gives an intense red coloration; sodium nitroprusside and potassium hydroxide provoke a deep red colour which changes to violet and finally disappears on the addition of acetic acid; ammonia and sodium nitroprusside impart a blue colour to the solution of the acid. S. S.

Nitric Esters of Hydroxy-acids. H. Duval (*Compt. rend.*, 1903, **137**, 571—573).—*Malic acid nitrate*, $CO_2H{\cdot}CH(O{\cdot}NO_2){\cdot}CH_2{\cdot}CO_2H$, prepared similarly to glycollic acid nitrate (Abstr., 1903, i, 603) by dissolving malic acid in a mixture of nitric acid of sp. gr. 1·45 and concentrated sulphuric acid, crystallises from a very small quantity of water in stellate clusters of white needles, which are not deliquescent; it melts and decomposes at 115°; dissolves in water, alcohol, ether, or acetic acid, and is insoluble in benzene or light petroleum.

Glyceric acid dinitrate, $NO_2{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}NO_2){\cdot}CO_2H$, is precipitated at −12° from a solution of glyceric acid in equal parts of fuming nitric and concentrated sulphuric acids; it crystallises from a mixture of ether and light petroleum (1 : 2) or from benzene in white crystals which decompose when kept at 117° for a few moments; it dissolves readily in water, alcohol, or ether, and is insoluble in light petroleum, chloroform, or carbon tetrachloride. M. A. W.

Solubility of Salts of the Alkaline Earths with Organic Acids in Acetic Acid. Walter Herz and G. Muhs (*Ber.*, 1903, **36**, 3715—3718).—The solubility of calcium, strontium, and barium tartrates and oxalates in acetic acid of various concentrations was determined at 26—27°. In all cases, the solubility is least in con-

centrated acetic acid, and exhibits a maximum between 2·5- and 3·5-normal, corresponding with the maximum of electrical conductivity between these concentrations. The purified salts, dried in a vacuum-desiccator, have the composition $CaC_4H_4O_6,4H_2O$; $SrC_4H_4O_6,3H_2O$; $BaC_4H_4O_6$; CaC_2O_4,H_2O; SrC_2O_4,H_2O; $BaC_2O_4,\frac{1}{2}H_2O$. C. H. D.

Cholic Acid. LODOVICO BECCARI (*Atti R. Accad. Torino*, 1903, **38**, 882—893).—Cholic acid crystallised from alcohol was obtained in the form of tetrahedra or octahedra having the composition $C_{24}H_{40}O_5,C_2H_6O$, which lose their alcohol of crystallisation at 110—115° and melt at 197°. The crystalline modification of the acid containing $1H_2O$, obtained by crystallising the moist acid from ether, is best dehydrated by heating for 2—4 hours at 115° under 600 mm. pressure. The anhydrous hexagonal prisms melting at 197° can only be prepared by boiling a saturated aqueous solution directly over the flame. The anhydrous acid has the molecular weight 407 in boiling acetone and 425 in boiling alcohol.

The *bromo*-derivative, $C_{18}H_{25}O_3Br$, obtained by the cautious addition of bromine to the dry powdered acid, separates from alcohol or ether in small, colourless prisms which melt and decompose at about 130° and dissolve in alkali carbonate solutions, by which, and also by alkali hydroxides, they are decomposed. T. H. P.

Synthesis of Tartaric Acid. SILVESTRO ZINNO (*L'Orosi*, 1902, **25**, 293—301).—After enumerating the known methods of synthesising tartaric acid and also some new ones, which are, however, only of theoretical significance, the author goes on to describe experiments made with the view of arriving at a method of synthesis which could be made use of in practice. He finds that the best results are obtained by just saturating glyceric acid of 26° B. at 15°, quite free from nitric acid, with potassium hydroxide solution of sp. gr. not greater than 1·134, the potassium glycerate thus formed being then treated with carbon dioxide under a pressure of 3 atmospheres. In this way, cream of tartar is obtained. This synthesis necessitated a means of preparing glyceric acid cheaply, which can be effected by heating a solution of glycerol, acidified with nitric acid, with lead dioxide or minium until decomposition is complete. The reactions in the two cases are expressed by the equations: (1) $2PbO_2 + 2C_3H_8O_3 + 4HNO_3 = Pb(NO_3)_2 + 5H_2O + Pb(C_3H_5O_4)_2 + NO + NO_2$; (2) $Pb_3O_4 + 2C_3H_8O_3 + 6HNO_3 = 2Pb(NO_3)_2 + Pb(C_3H_5O_4)_2 + 6H_2O + 2NO$. T. H. P.

Action of Methyl Chlorotricarballylate on Ethyl Sodiomalonate and Ethyl Sodioacetoacetate. W. BERTRAM (*Ber.*, 1903, **36**, 3291—3297).—Methyl aconitate, although failing to interact additively with hydrogen chloride, readily combines with hydrogen bromide to form *methyl β-bromotricarballylate*,

$$CO_2Me\cdot CBr(CH_2\cdot CO_2Me)_2,$$

which crystallises from ether in colourless needles, melts at 98—99°, and is easily decomposed on heating.

When methyl β-chlorotricarballylate, $CO_2Me\cdot CCl(CH_2\cdot CO_2Me)_2$, is condensed with methyl sodiomalonate (2 mols.) and the crystalline

sodium compound obtained carefully decomposed at 0° with hydrochloric acid, *methyl butane-aaβγδ-pentacarboxylate*,

$CH(CO_2Me)_2{\cdot}CH(CO_2Me){\cdot}CH(CO_2Me){\cdot}CH_2{\cdot}CO_2Me$,

is obtained; it crystallises from methyl alcohol and benzene in colourless needles and melts at 95—96°. The analogous *trimethyl diethyl* ester, $CH(CO_2Et)_2{\cdot}CH(CO_2Me){\cdot}CH(CO_2Me){\cdot}CH_2{\cdot}CO_2Me$, prepared by using ethyl instead of methyl sodiomalonate, crystallises from dilute alcohol in leaflets and melts at 57—58°. Both salts on hydrolysis give *n*-butane-*αβγδ*-tetracarboxylic acid (Auwers, Abstr., 1893, i, 253; 1894, i, 362). As the esters of a pentacarboxylic acid yielding *iso*butanetetracarboxylic acid, $CO_2H{\cdot}C(CH_2{\cdot}CO_2H)_3$, are not formed in the foregoing condensations, it is most probable that the sodiomalonic esters really react additively with methyl aconitate, formed from the chlorotricarballylate by the loss of hydrogen chloride. In like manner, methyl *β*-chlorotricarballylate and ethyl sodioacetoacetate give rise to *trimethyl ethyl α-acetyl-*n*-butane-αβγδ-tetracarboxylate*, $CO_2Et{\cdot}CHAc{\cdot}CH(CO_2Me){\cdot}CH(CO_2Me){\cdot}CH_2{\cdot}CO_2Me$, which crystallises from methyl alcohol and melts at 102°. W. A. D.

Citric Acid. Julius Meyer (*Ber.*, 1903, **36**, 3599—3601).—It has been suggested by Buchner and Witter (Abstr., 1892, 824) that there is a difference between the properties of aqueous solutions of hydrated and anhydrous citric acid, since the latter usually deposits anhydrous crystals. The hydrated acid separates, however, when a crystal of this form is added to the solution, and no difference can be detected between the densities or the conductivities of solutions prepared from the hydrated and the anhydrous acid. T. M. L.

New Method of Preparation of Aldehydes. Louis Bouveault (*Compt. rend.*, 1903, **137**, 987—989).—Béis has shown (this vol., i, 15) that amides react with magnesium alkyl haloids, but that the negative character of the hydrogen atoms in the NH_2 group causes a secondary reaction, which entirely prevents the formation of aldehydes in the case of formamide. Disubstituted derivatives of formamide, however, react normally according to the equation $NRR'{\cdot}CHO + MgXR'' = NRR'{\cdot}CHR''{\cdot}OMgX$, decomposing with water and dilute acids into $R''{\cdot}CHO$, $NHRR'$, and $MgX{\cdot}OH$. This method may be employed in the synthesis of a large number of aldehydes.

C. H. D.

Interaction between Formaldehyde and Silver Nitrate in presence of Strong Bases. Ludwig Vanino (*Ber.*, 1903, **36**, 3304—3305).—Silver is quantitatively separated from a solution containing silver nitrate (4 mols.), sodium hydroxide (6 mols.), and formaldehyde (2 mols.), whilst the filtrate contains sodium formate. The separation of silver is complete only when the sodium hydroxide is in excess. When both sodium hydroxide and formaldehyde are in large excess, a considerable evolution of hydrogen takes place; the action is catalytic. A. McK.

Propargylaldehyde [Propiolaldehyde] and Phenylpropargylaldehyde [Phenylpropiolaldehyde]. LUDWIG CLAISEN [and, in part, with PELTZ, STREITWOLF, and A. THOMASCHEWSKY] (*Ber.*, 1903, **36**, 3664—3373. Compare Abstr., 1898, i, 422).—The yield of these aldehydes by the action of alkali hydroxides on the corresponding acetals is not good, but in most reactions the acetals themselves may be employed in place of the aldehydes.

Hydroxylamine transforms propiolaldehyde into iso*oxazole*,

$$O<\begin{matrix}CH\colon CH \\ N{=}CH\end{matrix},$$

and not into the isomeric oxime. It is a colourless, mobile liquid, with a strong odour of pyridine, boils at 95—95·5° under 760 mm. pressure, and has a sp. gr. 1·0843 at 14°. It forms a *compound*, $2C_3H_3ON,PtCl_4$, in the form of yellow crystals, and a compound, $C_3H_3ON,CdCl_2$, as a colourless, crystalline powder. Alcoholic soda, or potassium ethoxide, transforms the *iso*oxazole into the *alkali* salt of *cyanovinyl alcohol*, ONa·CH:CH·CN, which reacts with benzenediazonium chloride yielding a *compound*, CHO·C(CN):N·NHPh, in the form of brownish-red, flat prisms melting at about 168°. The corresponding *anilide*, $NPh\colon CH\cdot CH_2\cdot CN$ or NHPh·CH:CH·CN, is colourless and melts at 124°.

Solutions of hydrazine sulphate and of phenylhydrazine hydrochloride convert the acetal of propiolaldehyde into pyrazole and 1-phenylpyrazole (compare Balbiano, Abstr., 1890, 797). Aniline forms an *additive* compound, CH:C·CH(OH)·NHPh, with the aldehyde; it melts at 122—123°, and, when boiled with an aqueous alcoholic solution of aniline hydrochloride, yields the compound $C_{15}H_{14}N_2,HCl$, probably the *hydrochloride* of the *dianilide* of *β-hydroxyacraldehyde*, NHPh·CH:CH·CH:NPh. The same product may be obtained by boiling the acetal of propiolaldehyde with an aqueous alcoholic solution of aniline hydrochloride. The free *base* crystallises in plates, melts at 115°, and yields sparingly soluble salts. When boiled with aqueous hydroxylamine hydrochloride, it yields *iso*oxazole.

When heated with sodium ethoxide at 100°, the acetal of propiolaldehyde combines with a molecule of ethyl alcohol yielding *β-ethoxyacraldehyde acetal*, $OEt\cdot CH\colon CH\cdot CH(OEt)_2$, as a colourless oil distilling at 190—193°. The same compound is obtained when Fischer and Giebe's ethoxybromopropiondehydracetal (Abstr., 1898, i, 168) is warmed with alcoholic potash. The β-ethoxy-acetal, when shaken with water, loses a molecule of alcohol and yields malondialdehyde, or the tautomeric β-hydroxyacraldehyde, which forms a *phenylazo*-derivative, $(C_3H_2O_2)\colon N\cdot NHPh$, melting at 116°.

Phenylpropiolaldehyde and ethyl malonate yield *ethyl phenylpropionylidenemalonate*, $CPh\colon C\cdot CH\colon C(CO_2Et)_2$, which, on warming with sulphuric acid, passes into *ethyl 6-phenyl-2-pyrone-3-carboxylate*,

$$CO_2Et\cdot C<\begin{matrix}CO{-}{-}O \\ CH\cdot CH\end{matrix}>CPh,$$ melting at 107—108°.

The *oxime* of phenylpropiolaldehyde melts at 108° and, on treatment with acetic anhydride, yields the nitrile of phenylpropiolic acid.

A small amount of alkali transforms it into the isomeric α-phenyl-*iso*oxazole; alcoholic sodium ethoxide at the ordinary temperature gives rise to cyanoacetophenone (Claisen and Stock, Abstr., 1891, 451).

γ-Substituted *iso*oxazoles are somewhat more stable towards alkali hydroxides, but ultimately furnish acetic acid and a nitrile, γ-phenyl-*iso*oxazole yielding benzonitrile and acetic acid. J. J. S.

Oxidation of β-Hydroxypropionacetal. Carl D. Harries (*Ber.*, 1903, **36**, 3658—3659).—A preliminary notice occasioned by the intimation of the publication of Claisen (preceding abstract). Just as methyl alcohol is oxidised by ozone to formaldehyde (Harries, Abstr., 1903, i, 605), β-hydroxypropionacetal, $OH\cdot CH_2\cdot CH_2\cdot CH(OEt)_2$, suffers oxidation to the half acetal of malondialdehyde,

$$CHO\cdot CH_2\cdot CH(OEt)_2.$$

The syrup, obtained by the oxidation of β-hydroxypropionacetal, reduced Fehling's solution when warmed gently, and yielded an oily phenylhydrazone; it could not, however, be distilled without decomposition until it had been converted into the acetal by Claisen's method, when a compound having the probable constitution,

$$CH(OEt)_2\cdot CH_2\cdot CH(OEt)_2,H_2O,$$

was obtained. On hydrolysis, this substance formed a phenylhydrazone melting above 200°, possibly malondialdehyde phenylhydrazone. A. McK.

Action of Mixed Organomagnesium Compounds on Amides. New Method of Preparing Ketones. Constantin Béis (*Compt. rend.*, 1903, **137**, 575—576).—Condensation between mixed organomagnesium compounds and acid amides occurs either at the NH_2 group or at both the CO and the NH_2 groups. Condensations of the latter type give a product which is decomposed by water yielding a ketone, according to the equations:

(1) $R\cdot CO\cdot NH_2 + 2MgR'X = CRR'(NHMgX)\cdot OMgX + R'H$;

(2) $CRR'(NHMgX)\cdot OMgX + 2H_2O = NH_2\cdot CRR'\cdot OH + MgX_2 + Mg(OH)_2$; (3) $NH_2\cdot CRR'\cdot OH = R\cdot CO\cdot R' + NH_3$, where X is a halogen radicle. The following ketones were thus prepared: methyl ethyl ketone from acetamide and magnesium etho-bromide or -iodide; diethyl ketone from propionamide and magnesium ethobromide; methyl propyl ketone from butyramide and magnesium methiodide; ethyl *iso*butyl ketone from *iso*valeramide and magnesium ethobromide; acetophenone from benzamide and magnesium methiodide; phenyl ethyl ketone from benzamide and magnesium ethiodide. The yield varies from 20 to 50 per cent., increasing with the complexity of the organic residue of the acid amide, thus, acetamide reacts only feebly with the organomagnesium compounds, and formamide does not react at all in the sense of the above equations. M. A. W.

Diacetone Alcohol and Mesityl Oxide. Moritz Kohn (*Monatsh.*, 1903, **24**, 765—772).—Diacetone alcohol [dimethylacetonylcarbinol] is oxidised by bromine and potassium hydroxide in aqueous solution to β-hydroxy*iso*valeric acid. With mesityl oxide, the oxidation results in the formation of ββ-dimethylacrylic acid. G. Y.

Action of Phosphorous Acid on Mannitol. Mannide. P. Carré (*Compt. rend.*, 1903, **137**, 517—520. Compare Abstr., 1903, i, 307 and 456, and Portes and Prunier, Abstr., 1902, i, 526).—When mannitol is heated with phosphorous acid at 125—130° under 18 mm. pressure, there is formed after one hour the *ester*, $C_4H_4(OH)_4[CH_2{\cdot}O{\cdot}P(OH)_2]_2$, the crystalline *calcium* salt of which was isolated. When the heating is continued for 3—4 hours, there is also produced, probably by interaction of the foregoing ester with excess of mannitol, a *monophosphorous ester* of *mannide*, $C_6H_9O_3{\cdot}O{\cdot}P(OH)_2$. Both these esters are monoacidic to helianthin and phenolphthalein, and are slowly hydrolysed by cold water.

Mannide readily reacts with phosphorus oxychloride at 50—60°, but is less readily esterified by phosphorous acid than mannitol, whence the author believes that Fauconnier's representation of mannide (Abstr., 1884, 1111) as a diprimary alcohol is inaccurate, the hydroxyls probably being present in secondary alcohol groups. The rates of esterification of mannitol and of mannide by phosphorous acid are tabulated in the original. T. A. H.

Hydrolysis of Substances containing Pentosans by Dilute Acids or by Sulphites. Isolation of Pentoses. Rudolf Hauers and Bernhard Tollens (*Ber.*, 1903, **36**, 3306—3322).—Few systematic investigations on the hydrolytic decomposition of naturally-occurring products, containing pentosans and yielding pentoses on hydrolysis, have been made and the authors have accordingly studied the hydrolysis of cherry-gum by hydrochloric and by sulphuric acids of varying concentrations. Figures are quoted to indicate how the rate of the hydrolysis varies with the strength of the acid used and with the time during which the various solutions are boiled. Hydrochloric acid acts more quickly than sulphuric acid of an equivalent strength, and this difference between the two acids is also shown in the difference of the reducing power of the products of hydrolysis. For the preparation of arabinose from cherry-gum, sulphuric acid is more convenient than hydrochloric acid, since it can be separated so easily by means of calcium carbonate.

A specimen of gum from La Plata, which contained much pentosan and little galactan, was hydrolysed with sulphuric acid. It yielded magnesium lactate, arabinose (identified by the formation of the phenylbenzylhydrazone and the bromophenylhydrazone), and xylose (identified by the phenylbenzylhydrazone). Whilst cherry-gum contains much araban and very little xylan, the gum from La Plata, on the other hand, contains about equal quantities of those two pentosans, together with very little galactan. A specimen of an East African gum, which contained 22·58 per cent. of galactan, gave arabinose on hydrolysis, but neither xylose nor galactose was isolated. A specimen of myrrh-gum yielded both arabinose and xylose; this gum contained much xylan and less araban

The method of hydrolysing gums by calcium sulphite is generally not so convenient as that by the mineral acids. Cherry-gum yielded arabinose but no xylose, whilst arabinose was also obtained from beet. Straw was found to contain much xylan and a little araban. Beech-

wood yielded xylose, but pine-wood gave very little arabinose and no xylose. When beet was hydrolysed by calcium sulphite, an acid having the composition $C_5H_{10}O_6$ was formed. When calcium sulphite is used, it is convenient to conduct the hydrolysis of the various substances containing pentosans at temperatures varying from 115° to 135°.

A. McK.

Hydrolysis of Starch by Acids. GEORGE W. ROLFE and H. W. GEROMANOS (*J. Amer. Chem. Soc.*, 1903, 25, 1003—1014).—It has been shown by Rolfe and Defren (Abstr., 1898, i, 7,) that in the products of the hydrolysis of starch by acids, a constant relation exists between the rotatory and cupric reducing powers. Brown, Morris, and Millar (Trans., 1897, 71, 115) have confirmed this observation, and have shown that a similar relation also exists in the fractions obtained by precipitating the hydrolysed product with alcohol.

In the present paper, a table is given containing the recalculated values of Rolfe and Defren's work, together with the results of an additional series of determinations. On plotting these figures, it is found that the reducing values do not lie on a straight line as they should if dextrose only were present. The results are, however, in substantial agreement with the original results of Rolfe and Defren, and prove that the products of the acid hydrolysis of starch contain another reducing substance in addition to dextrose. E. G.

Presence of Maltose in Acid-hydrolysed Starch Products. GEORGE W. ROLFE and ISAAC T. HADDOCK (*J. Amer. Chem. Soc.*, 1903, 25, 1015—1019).—It has been stated by Morris, Rolfe and Defren, and others that maltose is one of the products of the hydrolysis of starch by acids. A 15 per cent. solution of a specimen of commercial glucose, which had been obtained by hydrolysis with hydrochloric acid under a pressure of 2 atmospheres, was added drop by drop to 10 times its volume of 95 per cent. alcohol. As a result of this fractional precipitation, a product was obtained which, when treated with phenylhydrazine, yielded maltosazone identical in crystalline character and other properties with that obtained from pure maltose. E. G.

Transformation of Starch Paste. LÉON MAQUENNE (*Compt. rend.*, 1903, 137, 797—799. Compare Abstr., 1903, i, 679).—The author has examined the influence of temperature and of small quantities of mineral acids on the transformation of starch paste into amylocellulose, and finds (1) that the lower the temperature the more rapid and complete is the change, (2) the transformation is favoured by the presence of mineral acids (hydrochloric or sulphuric) even in quantities of $\frac{1}{10000}$, (3) the conversion tends towards a limit which at 0° and in a neutral medium appears to be at about 30 per cent.

M. A. W.

Rhodinamine. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1903, [iii], 29, 1046—1049).—*Rhodinamine*,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2,$$

obtained by reducing geranionitrile (Abstr., 1894, 83, and 1897,

537) with metallic sodium in presence of alcohol, is a colourless liquid with an odour simultaneously recalling that of fish and that of roses. It boils at 105° under 15 mm. pressure, and has a sp. gr. 0·839 at 0°/4°. The *salts* have a soapy appearance and are soluble in water, but are precipitated from their aqueous solutions by acids. Ethyl oxalate converts rhodinamine into a symmetrical disubstituted *oxamide*, which is crystalline and melts at 96°. When the amine, dissolved in moist ether, is treated with solid potassium hydroxide, it is converted into the corresponding *amino-alcohol*,

$$OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot NH_2,$$

by the assumption of a molecule of water. This is a viscid liquid, which boils at 140° under 15 mm. pressure and has a sp. gr. 0·910 at 0°/4°. The formation of rhodinamine affords no evidence as to whether the second ethylenic linking of geranionitrile occupies the $\alpha\beta$- or $\beta\gamma$-position. T. A. H.

Oxidation of Ethylenediamine. EUGEN BAMBERGER and RICHARD SELIGMAN (*Ber.*, 1903, **36**, 3831—3833).—When ethylenediamine hydrate is oxidised by Caro's acid, glyoxime is formed, thus :

$$C_2H_4(NH_2)_2 \longrightarrow [C_2H_4(NH\cdot OH)_2] \longrightarrow C_2H_2(N\cdot OH)_2.$$

The glyoxime was identified by its melting point, analysis, and the formation of hydroxylamine from it. The aqueous solution, from which the glyoxime had been removed, gave the ferric chloride reaction typical of hydroxamic acids. A. McK.

Action of Methylamine and Dimethylamine on Mesityl Oxide. ARMIN HOCHSTETTER and MORITZ KOHN (*Monatsh.*, 1903, **24**, 773—782. Compare Götschmann, *Annalen*, 1879, **197**, 27, 38; Sokoloff and Latschinoff, *Ber.*, 1874, **7**, 1387).—Methylamine and mesityl oxide form, almost quantitatively, an additive compound, which is probably methyldiacetonamine, $NHMe\cdot CMe_2\cdot CH_2\cdot COMe$, and not a compound of the constitution $CHMe_2\cdot CH(NHMe)\cdot COMe$. Similarly dimethylamine and mesityl oxide form, less easily (40 per cent. unchanged mesityl oxide), an additive compound which is considered to be dimethyldiacetonamine, $NMe_2\cdot CMe_2\cdot CH_2\cdot COMe$.

Methyldiacetonamine, which was not isolated, decomposes on distillation into mesityl oxide and methylamine; the *platinichloride*, $(C_7H_{15}ON)_2,H_2PtCl_6$, forms large, orange-red crystals. The *oxime* crystallises from light petroleum, melts at 57—59°, distils at 131° under 10 mm. pressure, and forms a *benzoyl* derivative which melts at 100—103° and an *oxalate*, $(C_7H_{16}ON)_2,C_2H_2O_4$, which crystallises from alcohol as a white powder.

Dimethyldiacetonamine, when heated, decomposes into dimethylamine and mesityl oxide. The *oxime* crystallises in white needles, sinters at 38—40°, and melts at 46—47°, boils at 136—138° under 17 mm. pressure, and forms an unstable *additive* compound with methyl iodide, and an *oxalate*, $(C_8H_{17}ON)_2,C_2H_2O_4$, which separates from alcohol as a white, hygroscopic powder. G. Y.

***iso*Glucosamine.** LÉON MAQUENNE (*Compt. rend.*, 1903, **137**, 658—660).—The glucamine series of bases, prepared by the author and

Roux (Abstr., 1901, i, 372 ; 1903, i, 73, 436) by the reduction of the aldosoximes by sodium amalgam, bear the same relation to the glucosamines as exists between the polyhydric alcohols and the reduced sugars, the one passing into the other by the addition of hydrogen. Thus, when *iso*glucosamine is reduced by means of sodium amalgam in an alkaline solution, two stereoisomeric bases belonging to the glucamine series are produced, *d*-mannamine (identified by means of its oxalate melting at 186° with the salt prepared expressly for the purpose by Roux, by the reduction of mannosoxime), and *d*-glucamine. This fact confirms the presence of a ketonic grouping in *iso*glucosamine, and furnishes a means of passing from the mannitol to the sorbitol series and conversely. M. A. W.

Ethyl β-Diethylaminopropionate. BERNHARD FLÜRSCHEIM (*J. pr. Chem.*, 1903, [ii], 68, 345—356).—Ethyl β-iodopropionate is best prepared by heating β-iodopropionic acid with alcohol and sulphuric acid (Otto, Abstr., 1888, 360). If hydrochloric acid is used (Harries and Loth, Abstr., 1896, i, 321), part of the iodine is replaced by chlorine.

Ethyl β-diethylaminopropionate, formed by the action of an excess of diethylamine on ethyl β-iodopropionate, is a colourless liquid, which boils at 192° under 753 mm., and at 83—84° under 12 mm. pressure, and has a characteristic amine odour. It is moderately soluble in water, and easily in dilute hydrochloric acid, from its solution, in which it is quantitatively recovered by addition of sodium carbonate and extraction with ether. It is easily hydrolysed by dilute hydrochloric acid, even at the ordinary temperature. Addition of mercuric chloride to the aqueous solution of the ester produces a voluminous yellow precipitate, which quickly becomes scarlet, and is dissolved by sulphuric acid. The *hydrochloride* is very hygroscopic.

Diethylamine hydriodide, formed along with ethyl β-diethylaminopropionate, crystallises in colourless needles, melts at 168—170°, is not deliquescent, and dissolves easily in water or alcohol, but is only slightly soluble in benzene or ether. The action of ethyl β-diethylaminopropionate on ethyl β-iodopropionate in ethereal solution leads to the formation of ethyl acrylate, diethylamine hydriodide, and the *hydriodide* of ethyl β-diethylaminopropionate, which deliquesces on exposure to the atmosphere, and at 165° decomposes with formation of ethyl acrylate. Ethyl β-diethylaminopropionate is formed when ethyl acrylate is boiled with an excess of diethylamine.

β-Diethylaminopropionic acid, obtained from the ester by hydrolysis with dilute hydrochloric acid, is colourless, melts at 70—71°, is very hygroscopic, is easily soluble in water or alcohol, and insoluble in ether, has an acid reaction in aqueous solution, and is not decomposed by boiling aqueous sodium hydroxide. At 160°, the acid decomposes with formation of *diethylamine acrylate,* which evolves diethylamine when warmed with aqueous sodium hydroxide. On distillation of the diethylamine acrylate, there remains a colourless residue which is soluble in aqueous alkalis and is probably a polymerisation product of acrylic acid. *Ethyl sodio-β-diethylaminopropionate* is formed by the action of granulated sodium on the ester in ethereal solution; it is

decomposed by the action of water, glacial acetic acid, or hydrogen chloride, the chief products being unchanged ester and diethylamine. The action of benzyl chloride on the sodio-compound leads to the formation of benzyldiethylamine hydrochloride. From the products of the reaction between benzoyl chloride and the sodio-compound, there have been separated, unchanged ester, diethylamine, diethylbenzamide, ethyl benzoate, benzoic anhydride, a solid, brown substance which is soluble in alcohol or aqueous hydrochloric acid, and a basic oil which yields a yellow *platinichloride*.

Tetraethyltrimethylenediamine, formed by the action of trimethylene dibromide on diethylamine in toluene solution, is a colourless oil, which boils at 205—209°, has a characteristic odour, and, with mercuric chloride in aqueous solution, gives a colourless precipitate which rapidly becomes yellow and, finally, olive-green. The *mercurichloride*, $C_3H_6(NEt_2)_2,2HCl,2HgCl_2$, crystallises in colourless, monoclinic prisms and melts at 124—125°.

Tetraethyltrimethylenediamine does not react with potassium, sodium, or benzoyl chloride. G. Y.

Action of Hydrogen Cyanide on Aldehyde-ammonia and Analogous Compounds. Marcel Delépine (*Compt. rend.*, 1903, **137**, 984—986).—The equations generally assumed for the synthesis of amino-acids from aldehyde-ammonias and hydrogen cyanide cannot be applied to the reactions between hydrogen cyanide and ethylideneimine or methylmethyleneamine. The hydrogen cyanide is added to the molecule at the double linking, as in the equations $CHMe{:}NH + HCN = CN{\cdot}CHMe{\cdot}NH_2$ and $CHMe{:}NR + HCN = CN{\cdot}CHMe{\cdot}NHR$. In many cases, the reaction is complicated by the polymerisation of the amino-nitriles first formed. C. H. D.

Action of Potassium Thiocyanate on Ammonium Heptamolybdate. I. C. Reichard (*Chem. Zeit.*, 1903, **27**, 1134—1135).—When potassium thiocyanate and a little hydrochloric acid are added to a solution of molybdic acid, an intense yellow coloration is produced, which disappears on the addition of ammonia or of potassium hydroxide solution, and is regenerated when the colourless solution is acidified. When a strong solution of potassium thiocyanate is added to a very dilute solution of ammonium molybdate, the solution, after 24 hours, deposits a white precipitate. When strong solutions of potassium thiocyanate and ammonium molybdate are mixed, the separation of this white compound takes place immediately. Alkaline tungstate solutions do not form a precipitate with potassium thiocyanate. By the action of potassium thiocyanate on ammonium molybdate, two distinct compounds of molybdenum and thiocyanic acid are formed. A. McK.

Iodocyanides of Potassium and Cæsium. C. H. Mathewson and Horace L. Wells (*Amer. Chem. J.*, 1903, **30**, 430—432).—By dissolving iodine in a concentrated solution of potassium cyanide, Langlois (*Ann. Chim. Phys.*, 1860, [iii], **60**, 220) obtained a compound to which he assigned the formula $KI,4CNI,4H_2O$. It is now found that this salt contains only $1H_2O$. No evidence was obtained of the

existence of any other compound of the iodides of potassium and cyanogen.

Cæsium iodocyanide, CsI,2CNI, forms cinnamon-coloured, orthorhombic plates, and is sparingly soluble in water. This is the only double salt of cæsium and cyanogen iodides which could be obtained.

E. G.

Compound of Mercuric Cyanide and Cæsium Iodide. C. H. Mathewson and Horace L. Wells (*Amer. Chem. J.*, 1903, 30, 432—433).—Mercuric cyanide combines with cæsium iodide in only one proportion forming the *compound*, $CsI,Hg(CN)_2$, which crystallises in white, pearly plates, and is decomposed by acids with formation of hydrogen cyanide and mercuric iodide. It can be recrystallised readily from water, and remains unchanged in composition. E. G.

Chemical Equilibrium Between Hydroferrocyanic and Hydroferricyanic Acids. Maurice Prud'homme (*Bull. Soc. chim.*, 1903, [iii], 29, 1009—1010).—The author finds that solutions of hydroferricyanic acid give a blue coloration with filter papers impregnated with guaiacum tincture, and that consequently this indicator cannot be used to determine the end-point in the titration of ferrocyanides with chromic acid solutions. This change is a reversible one, and the titration liquid acquires the property of giving a blue colour with guaiacum at the equilibrium point. If the titration is continued beyond this point until the liquid no longer gives a blue colour with filter paper (due to the latter containing traces of chlorine introduced in bleaching the pulp), then the conversion of hydroferrocyanic into hydroferricyanic acid is complete. Measurement of the volumes of chromic acid solutions requisite to produce (*a*) equilibrium and (*b*) complete conversion, indicate that the relative velocities of the oxidising and deoxidising reactions are as 10 : 1. A process is given for estimating soluble ferrocyanides by titration with chromic acid, based on these observations. T. A. H.

Chemical Equilibrium between Potassium Ferrocyanide and Ferricyanide in presence of Alkali Hydroxides. Maurice Prud'homme (*Bull. Soc. chim.*, 1903, [iii], 29, 1010—1012).—Potassium ferricyanide is converted into potassium ferrocyanide by prolonged ebullition of its aqueous solutions in presence of alkali hydroxides, but the reduction is complete only in presence of reducing agents, for instance, dextrose and indigotin. The rapidity of oxidation of indigotin by ebullition with solutions containing sodium hydroxide and potassium ferricyanide is directly proportional to the concentration of these two substances in the solutions, but in presence of these and of potassium ferrocyanide the rate becomes inversely proportional to the concentration of the ferrocyanide.

It is suggested that when solutions containing potassium ferricyanide and hydroxide are boiled, equilibrium is reached in the reversible reaction $K_6Fe_2Cy_{12} + 2KOH \rightleftarrows 2K_4FeCy_6 + H_2O_2$. In conformity with this view it was observed that (*a*) potassium ferricyanide and hydroxide are formed when a solution of hydrogen peroxide is added to one of

potassium ferrocyanide, (*b*) the addition of excess of hydrogen peroxide to a solution containing potassium ferricyanide and sodium hydroxide results eventually in the formation of potassium ferrocyanide and the evolution of oxygen, and (*c*) the bleaching of indigotin by hydrogen peroxide is much more rapid in presence of an alkali hydroxide than in acid solution. T. A. H.

Systematic Alkylation of Arsenic. VICTOR AUGER (*Compt. rend.*, 1903, **137**, 925—927).—By an extension of Meyer's method of methylating sodium arsenite (Abstr., 1883, 1078), the author has obtained arsenious compounds containing one, two, or three methyl groups. Sodium monomethylarsonate, $AsMeO(ONa)_2$, is reduced by sulphur dioxide to methylarsenoxide, AsMeO, which, in the form of its disodium derivative, $AsMe(ONa)_2$, reacts readily with methyl iodide to give the sodium derivative of cacodylic acid, $AsMe_2O{\cdot}ONa$; the reduction of this compound yields cacodyl oxide, the sodium derivative of which, $AsMe_2{\cdot}ONa$, reacts with methyl iodide to form the oxide of trimethylarsine, $AsMe_3O$.

Attempts to prepare the corresponding ethyl derivatives have been less successful, and not yet carried beyond the stage of ethylarsonic acid, $AsEtO(OH)_2$. M. A. W.

Inorganic Additive Compounds of Unsaturated Substances. JULIUS SAND (*Annalen*, 1903, **329**, 135—166).—The compounds of mercury salts with ethylene and its derivatives, the compounds of cobaltous ammonium salts with oxygen, and the compounds of cobaltic ammonium salts with nitric oxide are discussed in this paper.

A summary of the chief compounds obtained from mercury salts and ethylene derivatives is given, the substances prepared from unsaturated alcohols and oximes being considered in detail; it is pointed out that only the simple ethylene linking is capable of forming an additive compound with mercury salts, whilst a conjugated pair of ethylene linkings, which will take up bromine, and the ethylene linkings in benzene, which will not combine with bromine, are neither of them able to combine with mercury salts.

Attention is drawn to the fact that these organo-mercury compounds behave very differently towards different acids, &c.; thus they are immediately decomposed by hydrochloric and hydrobromic acids and by potassium cyanide, an ethylene linking being regenerated; for example, mercuryethanol bromide yields ethylene. Nitric and sulphuric acids are without action on these substances. It would appear that mercury compounds of this type can only be decomposed by reagents which will form complex negative ions with the mercury, as, for example, $(HgCl_4)$, or $(HgSCN_4)$. It is suggested that in these complex mercury ions the mercury atom is quadrivalent, but that two of the valencies are of a different order from the others. Further, it is possible that two series of mercuryethanol salts exist; in one, the metal is quadrivalent, and is linked with the partial valencies of the ethylene, whilst in the other the linkage is represented by the formula $IHg{\cdot}CH_2{\cdot}CH_2{\cdot}OH$; acids and other compounds which are capable of forming a complex ion with the mercury bring about the

conversion of the latter compound into that first mentioned, $\begin{matrix} CH_2 \cdots \\ \| \\ CH_2 \cdots \end{matrix} > Hg < \begin{matrix} I \\ OH \end{matrix}$.

The addition of oxygen and nitric oxide to cobaltamines is discussed at considerable length; the author sees in both phenomena the exhibition of "partial" or subsidiary valency in the molecule of oxygen and nitric oxide. K. J. P. O.

Action of Mercuric Salts on Unsaturated Alcohols and Oximes. Julius Sand and Fritz Singer (*Annalen*, 1903, 329, 166—194. Compare Abstr., 1902, i, 851 and preceding abstract).—Dimethylheptenol, prepared from methylheptenol (*loc. cit.*), readily reacts with aqueous mercury acetate, forming a solution from which alkaline potassium iodide precipitates two pairs of isomeric iodides. One pair of *iodides* are soluble in alkali hydroxides, and have the constitution

$$OH \cdot CMe_2 \cdot CH(HgI) \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH.$$

The *α-form* is a solid melting at 124—125°, and differs from the *β*-form in solubility and stability towards acids. The other pair of *iodides* are cyclic compounds, $HgI \cdot CH < \begin{matrix} CMe_2 - O \\ CH_2 \cdot CH_2 \end{matrix} > CMe_2$, and are prepared by shaking the heptenol with aqueous mercury acetate, adding 10 per cent. potassium hydroxide to the clear solution, and then introducing aqueous potassium iodide; the *β-iodide* of mercuridimethylheptene oxide separates as an oil, extremely soluble in alcohol, but only slowly acted on by alkalis. The *α-iodide* is prepared in the same manner as the *β*-compound, and separates as a solid containing the *β*-form, which is extracted by treatment with cold alcohol; the pure substance forms white crystals melting at 108—110°, and is the stable form as the *β*-form slowly changes into it in the presence of alkali, the reverse transformation never taking place.

The *β-iodide* of the mercuriheptanediol,

$$OH \cdot CMe_2 \cdot CH(HgI) \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH,$$

is precipitated in the form of an oil by carbon dioxide from the alkaline liquor from which the insoluble cyclic iodides have separated. It is transformed into the stable *α-modification* either when its benzene solution is boiled or by keeping its alkaline solution for several weeks; the *α-iodide* forms well-developed crystals melting and decomposing at 124—125°, and is less soluble in benzene or alkali than the *β*-modification.

Ethylhexenol, $CH_2{:}CH \cdot [CH_2]_2 \cdot CMeEt \cdot OH$, is prepared by the action of ethyl bromide on allylacetone in the presence of magnesium powder and is a liquid boiling at 65° under 14 mm. pressure; it dissolves readily in aqueous mercuric acetate; from the solution, alkaline potassium iodide precipitates an oil, the separation of which is completed by passing in carbon dioxide; after treatment with ether, a crystalline substance is obtained melting at 44°, and is probably a tetrahydrofurfuran derivative, $\begin{matrix} CH_2 \text{———} CMeEt \\ | \\ CH_2 \cdot CH(CH_2 \cdot HgI) \end{matrix} > O$, since under the action of iodine, an oily iodide is formed, which is shown by treatment with permanganate to be saturated; when it is oxidised by chromic

acid, an aldehyde is produced. Hydrochloric acid converts the original mercuri-iodide back into ethylhexenol.

Allylacetoxime (an oil boiling at 190° under 720 mm. pressure) reacts with mercury acetate to form a *hydroisooxazole* derivative,

$$HgI\cdot CH_2\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ O\text{———}N\end{matrix}>CMe,$$

which is purified by washing with ether and recrystallising from alcohol, when it melts at 122°.

Methylheptenoneoxime yields several hydrogenated *iso*oxazole derivatives according as the reaction between the mercury salt and the oxime takes place in acid or alkaline solution. When the oxime is treated with mercury acetate in acid solution and the resulting product precipitated with potassium iodide, a mixture of two *substances* is obtained, which can be separated by treatment with cold alcohol, in which the one is soluble, whilst the other is not; the soluble substance, the α-modification, forms white crystals melting at 94°, the other is a yellow, crystalline solid and melts at 123°; they are probably both represented by the constitution

$$HgI\cdot CH<\begin{matrix}CMe_2\text{—}O\text{—}NI\cdot HgI\\ CH_2\cdot CH_2\cdot CMe\end{matrix}.$$

The substance melting at 94° yields a *picrate* (probably an oxonium picrate), $(C_8H_{14}ONHg_2I_3)_2,C_6H_3O_7N_3$, which is crystalline, sinters at 65° and melts at 78—80°. When potassium bromide is substituted for potassium iodide in the preparation of the *iso*oxazole derivative, a *bromide*, $C_8H_{14}ONBr_3Hg_2$, is obtained as white crystals melting at 123°; both the iodides and the bromide are soluble in alkali hydroxides without precipitation of mercury oxide, and under the influence of hydrazine, in the presence of alkali, lose half their mercury, which is precipitated as metal.

When the interaction of the ethylhexenol and mercury acetate takes place in the presence of potassium hydrogen carbonate, an oil separates on addition of potassium iodide, and is converted into a crystalline solid on repeated solution in methyl alcohol and precipitation with ether; this substance, $(C_8H_{14}ONIHg)_2,HgI_2$, melts and decomposes at 150°; in the mother liquors, a more soluble isomeride, the *α-form*, is found, and can be obtained as a crystalline powder melting at 114°.

Mercuryethanol bromide can be converted by evaporation with acetic anhydride into an *acetyl* derivative, $HgBr\cdot CH_2\cdot CH_2\cdot OAc$, which crystallises in lustrous leaflets melting at 75°. When treated with hydrochloric acid, ethylene is evolved. When oxidised by permanganate, the ethanol bromide is mainly converted into oxalic acid, the *bromide* of mercuriacetic acid, $HgBr\cdot CH_2\cdot CO_2H$, being at the same time produced; it crystallises in colourless needles melting at 198°, and is not decomposed by hydrochloric acid. K. J. P. O.

Mercury Compounds of Ketones. Julius Sand and Otto Genssler (*Ber.*, 1903, 36, 3699—3706).—When mercuric acetate is heated with acetone under pressure at 100°, a crystalline compound, $C_6H_{10}O_3Hg_4(C_2H_3O_2)_4$, is formed, which can be recrystallised from

alcohol to which a drop of acetic acid has been added; it melts at 157° and probably has the following constitution:

$$CH(Hg\cdot OAc)_2\cdot CMe(OH)\cdot O\cdot CMe(OH)\cdot CH(Hg\cdot OAc)_2;$$

potassium hydroxide converts this acetate into an insoluble *oxide*, $C_6H_{10}O_5Hg_4$.

Methyl ethyl ketone forms a similar oxonium compound with mercuric acetate, which combines with $\frac{1}{2}$ mol. of picric acid.

Dihydronaphthalene forms with mercuric acetate an *acetate*, crystallising either from benzene or light petroleum in long needles melting at 122°. This is soluble in potassium hydroxide; potassium bromide precipitates the corresponding *bromide*, which crystallises from benzene in white, glistening needles melting at 159°. The *iodide* is also insoluble in alkali; it melts at 156°. E. F. A.

Mercuric Acetate and Acetic Anhydride. JULIUS SAND and FRITZ SINGER (*Ber.*, 1903, 36, 3707—3710).—On heating mercuric acetate with freshly distilled acetic anhydride at the temperature of the water-bath, it gradually goes into solution, forming a complicated mercury derivative of acetic acid, $O<{Hg \atop CO}>C(Hg\cdot OAc)_2$. This *acetate* is insoluble in organic solvents, dissolves and decomposes in hydrogen chloride solutions, but is soluble in cold 20 per cent. nitric acid; on precipitation with much water, a *nitroacetate*, ${OAc\cdot Hg \atop NO_3Hg}>C<{Hg \atop CO}>O$, is formed. Both these compounds are non-explosive, but the free base, prepared by decomposing the diacetate with cold potassium hydroxide is an exceedingly explosive compound. It is colourless, easily soluble in cold 20 per cent. hydrochloric acid or in potassium cyanide solution, and has the constitution $O<{Hg \atop Hg}>C<{Hg \atop CO}>O,2\frac{1}{2}H_2O$. When heated at 160°, it loses carbon dioxide and water, forming probably a methane derivative,

$$O<{Hg \atop Hg}>C:Hg;$$

reduction with sodium amalgam converts it into silver acetate, whilst potassium iodide forms the corresponding iodide. E. F. A.

New Synthesis of Hydrocarbons by means of Organo-magnesium Compounds. ALFRED WERNER (*Ber.*, 1903, 36, 3618—3619).—A question of priority (see Houben, Abstr., 1903, i, 805, and Werner and Zilkens, *ibid.*, 615). C. H. D.

Hydrides of Cyclic Hydrocarbons. JOHANN F. EIJKMAN (*Chem. Centr.*, 1903, ii, 989; from *Chem. Weekblad.*, 1, 7—12).—The following cyclic hydrocarbons have been prepared by Sabatier and Senderens' method of forming hydro-compounds in presence of nickel. *Tricyclodecane*, $CH_2<{CH_2\cdot CH\cdot CH\cdot CH_2 \atop CH_2\cdot CH\cdot CH\cdot CH_2}>CH_2$, obtained from dicyclopentadiene, crystallises from alcohol or glacial acetic acid, melts at 77°,

boils at 86° under 24 mm., at 123° under 100 mm., or at 193° under 769 mm. pressure, and has a sp. gr. 0·9120 at 80°; it has a taste and odour similar to those of camphor, and is not attacked by concentrated sulphuric acid, but by prolonged heating with concentrated sulphuric acid and a small quantity of pyrosulphuric acid at a temperature a little above the melting point, it forms an isomeride which melts at about 9°, boils at 191·5° under 769 mm. pressure, and has a sp. gr. 0·9021 at 80°. These substances are probably cis- and trans-stereoisomerides. Cyclo*pentane*, C_5H_{10}, prepared from *cyclo*pentadiene, is liquid at −80°, boils at 49° under 760 mm. pressure, and has a sp. gr. 0·7517 at 12·7°.

Hydrindene yields *dic*yclo*nonane*, $\begin{matrix} CH_2\cdot CH_2\cdot CH\cdot CH_2 \\ CH_2\cdot CH_2\cdot CH\cdot CH_2 \end{matrix}\!>\!CH_2$, which boils at 163—164° and has a sp. gr. 0·8759 at 23°. *Di*cyclo*tridecane* (*dodecahydrodiphenylmethane*), $C_6H_{11}\cdot CH_2\cdot C_6H_{11}$, prepared from diphenylmethane, boils at 150° under 45 mm. or at 251·5° under 760 mm. pressure, and has a sp. gr. 0·8765 at 19·7°; it crystallises from its solution in ether when cooled by means of alcohol and carbon dioxide. Diphenyl yields *phenyl*cyclo*hexane*, $C_6H_5\cdot C_6H_{11}$, which melts at about 0°, boils at 106° under 12 mm., at 156° under 80 mm., or at 238° under 770 mm. pressure, and has a sp. gr. 0·9306 at 17·1°.

E. W. W.

Action of Nascent Acetylene on Benzene in presence of Aluminium Chloride. E. Parone (*L'Orosi*, 1902, 25, 148—153).—The action of nascent acetylene on benzene in presence of aluminium chloride, when allowed to continue for several days, during which the aluminium chloride and calcium carbide were frequently renewed, was found to yield mainly ethylbenzene, styrene, dibenzyl, and anthracene. The formation of these compounds is explained by Friedel and Craft's theory of the action of aluminium chloride in organic syntheses.

T. H. P.

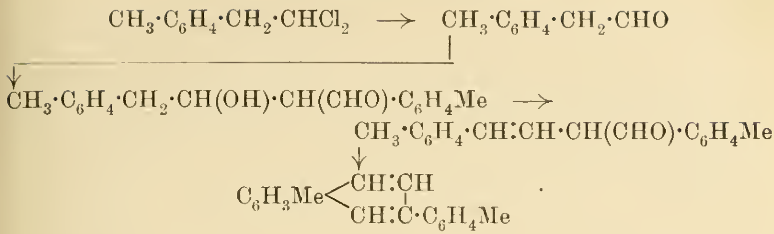
Cyclic Ketones from Chloroform and Phenols. Karl Auwers and G. Keil (*Ber.*, 1903, 36, 3902—3911).—The substance $C_9H_{10}Cl_2$, obtained by the elimination of water from the compound

$$CHCl_2\cdot CMe<\begin{matrix} CH:CH \\ CH:CH \end{matrix}>CMe\cdot OH$$

(Abstr., 1903, i, 620), on oxidation with chromic acid in acetic acid solution gives $\beta\beta$-dichloro-*p*-ethylbenzoic acid, and is therefore p-*methyl-$\beta\beta$-dichloroethylbenzene*, $CH_3\cdot C_6H_4\cdot CH_2\cdot CHCl_2$.

*$\beta\beta$-Dichloro-*p*-ethylbenzoic acid*, $CHCl_2\cdot CH_2\cdot C_6H_4\cdot CO_2H$, crystallises from benzene in slender, white needles, melts at 179—181°, and on reduction with sodium dissolved in alcohol gives *p*-ethylbenzoic acid.

The hydrocarbon, $C_{18}H_{16}$, obtained by the action of water at a high temperature on *p*-methyl-$\beta\beta$-dichloroethylbenzene is shown to be 3-*methyl*-6-p-*tolylnaphthalene* by the following considerations; its formation from *p*-methyl-$\beta\beta$-dichloroethylbenzene may therefore be expressed as follows:



p-*Methyl-β-chlorostyrene*, $C_6H_4Me\cdot CH\!:\!CHCl$, prepared either by heating the chloride, $C_9H_{10}Cl_2$, with alcoholic potassium hydroxide, or synthetically by adding a solution of sodium carbonate saturated with chlorine to an alkaline solution of *p*-methylcinnamic acid and subsequently distilling the additive compound,

$$C_6H_4Me\cdot CH(OH)\cdot CHCl\cdot CO_2H,$$

formed, with dilute sulphuric acid, crystallises from methyl alcohol in slender, white needles, melts at 36—37°, and boils at 128—134° under 38—41 mm. or at 222—224° under the ordinary pressure. The analogous p-*methyl-β-bromostyrene*, $C_6H_4Me\cdot CH\!:\!CHBr$, crystallises from methyl alcohol in long prisms and melts at 46·5—47·5°. When either of the foregoing compounds is heated with water for 3 hours at 170—180°, the hydrocarbon, $C_{18}H_{16}$, is obtained.

β-Phenylacetaldehyde (compare Zincke and Breuer, Abstr., 1885, 269) is easily converted into β-phenylnaphthalene by heating it with dilute hydrochloric acid for 3 hours at 170—180°; the same substance is formed by similarly treating β-chlorostyrene. ββ-Dichloroethylbenzene, $CH_2Ph\cdot CHCl_2$, has been described by Forrer (Abstr., 1884, 1020) as decomposing spontaneously at the ordinary temperature, but the authors have prepared it by the action of phosphorus pentachloride on phenylacetaldehyde, and find that it boils at 110—119° under 25 mm. or at 210—220° under 760 mm. pressure without decomposition occurring; it has a sp. gr. 1·153 at 18°.

β-Phenylacetaldehydesemicarbazone crystallises from dilute alcohol in small, thick prisms and melts at 153°. W. A. D.

Amylbenzenes. AUGUST KLAGES (*Ber.*, 1903, **36**, 3688—3694. Compare Abstr., 1903, i, 19).—α-Methylbutylbenzene [*sec.*-Amylbenzene], $CHMePh\cdot CH_2\cdot CH_2Me$, is easily soluble in sulphuric acid containing 6 per cent. of sulphur trioxide, forming a *sulphonic acid* which yields crystalline *sodium* and *barium* ($+H_2O$) salts; the *sulphonic chloride* is a clear, viscous oil boiling at 194° under 12 mm. pressure and having a sp. gr. 1·1751 at 15°/4° and n_D 1·5308. The *amide* crystallises from light petroleum in glistening needles and melts at 66—67°, the *benzylamide* melts at 62—64°, and the *anilide* forms well-defined prisms melting at 60—61°.

Phenylmethylisopropylcarbinol, $CMePr^{\alpha}Ph\cdot OH$, produced by the interaction of *iso*butyrylbenzene and magnesium methiodide in the cold, is a colourless, viscid oil boiling at 109—110° under 12 mm. or at 196—198° under atmospheric pressure, and having a sp. gr. 0·9653 at 13·5°/4° and n_D 1·51611. The corresponding *chloride* is a colourless

oil having an odour of cymene and losing hydrogen chloride when heated.

α-iso*Propylvinylbenzene* [*β-phenyl-Δ^{α}-amylene*], $CH_2{:}CPrPh$, obtained by heating the chloride with pyridine, is an oil boiling at 82° under 12 mm. or at 191—192° under 753 mm. pressure, and having a sp. gr. 0·8991 at 13·8°/4° and n_D 1·5181; it forms an oily *dibromide*. When reduced with sodium and alcohol, it is converted into *αβ-dimethylpropylbenzene* [sec.-iso*amylbenzene*], $CHMePh{\cdot}CHMe_2$, boiling at 188—189° and having a sp. gr. 0·8672 at 16°/4° and n_D 1·4972; it dissolves in sulphuric acid, the *barium* salt of the *sulphonic acid* crystallising (with $2H_2O$) in glistening plates.

Phenyldiethylcarbinol is a colourless, viscid oil boiling at 107—109° under 14 mm. or at 223—224° under atmospheric pressure; it has a sp. gr. 0·9706 at 12·5°/4°, and n_D 1·51665. The *chloride* is a colourless, odourless oil; it is converted on heating with pyridine into *α-ethylpropenyl benzene* [*γ-phenyl-Δ^{β}-amylene*], $CEtPh{:}CHMe$, a colourless oil with a strong cymene-like odour, boiling at 91—93° under 18 mm. or at 197—198° under 753 mm. pressure, and having a sp. gr. 0·9173 at 14°/4° and n_D 1·5266. It unites with bromine and forms a *nitrosochloride* melting at 117°. On reduction, it forms α-ethylpropylbenzene [phenyldiethylmethane], $CHEt_2Ph$, which boils at 73—74° under 12 mm. or at 187° under 753 mm. pressure, and has a sp. gr. 0·8755 and n_D 1·4988. The *sulphonic acid* forms a barium salt crystallising with H_2O and a *sulphonamide* crystallising from alcohol in glistening plates or needles melting at 89—90°. These constants are slightly different from those given by Dafert (Abstr., 1883, 659).

E. F. A.

Influence of Sulphur and of Sulphur-containing Groups on the Order of Substitution of Hydrogen Atoms in Cyclic Nuclei. Sulphur Derivatives of Phenyl Sulphide. EDOUARD BOURGEOIS and KARL PETERMANN (*Rec. trav. chim.*, 1903, 22, 349—355 and 356—366).—When phenyl sulphide is dissolved in sulphuric acid at 15°, a mixture of thiodibenzenedi-*o*-sulphonic acid and its *para*-isomeride is formed, whilst the latter only is produced when the solution is effected at 100° (compare Krafft, Abstr., 1875, 153, and Otto and Tröger, Abstr., 1893, 416). The two acids can be separated most readily by conversion into the corresponding chlorides and fractional crystallisation of the mixed chlorides from benzene.

Thiodibenzenedi-*p*-sulphonic acid, $S(C_6H_4{\cdot}SO_3H)_2$, crystallises in masses of tangled lamellæ and is very hygroscopic. The corresponding chloride, obtained by the action of phosphorus pentachloride on the potassium salt of the acid, crystallises from benzene in colourless prisms and melts at 159° (compare Otto and Tröger, *loc. cit.*); it is readily hydrolysed by methyl or ethyl alcohol, regenerating the acid and forming methyl or ethyl ether, but not by water. When dry methyl alcohol is treated with one third of its weight of the chloride at 15°, *methyl thiodibenzenedi*-p-*sulphonate* is formed; this crystallises in brilliant prisms and at first melts at 97°, but after preservation for some weeks the melting point rises to 118° and then

remains constant even after recrystallisation. The two forms of the methyl ester yield the original acid on hydrolysis.

Thiodibenzenedi-p-*sulphonamide*, $S(C_6H_4\cdot SO_2\cdot NH_2)_2$, prepared by the action of excess of ammonium carbonate on the chloride at 80°, forms colourless, crystalline crusts, melts at 195°, and is sparingly soluble in the usual solvents; the corresponding *sulphonanilide*, similarly prepared, crystallises from boiling alcohol in silky, prismatic needles and melts at 212·5°.

Thiodibenzenedi-p-*sulphinic acid*, $S(C_6H_4\cdot SO_2H)_2$, prepared by reducing the disulphonic chloride, dissolved in benzene, with moist zinc dust, crystallises in brilliant leaflets, decomposes between 107° and 110°, and on reduction with zinc and hydrochloric acid furnishes the corresponding *di*-p-*thiol*, $S(C_6H_4\cdot SH)_2$; this crystallises from alcohol in brilliant spangles, melts at 116·5°, and boils at 147·5—148·5° under 11·5 mm. pressure: the *lead mercaptide* is an orange-yellow precipitate which decomposes at 278°, the *methyl thio-ether*, $S(C_6H_4\cdot SMe)_2$, prepared by the interaction of methyl iodide with the sodium derivative of the dithiol, forms large, brilliant lamellæ and melts at 89°. When the lead mercaptide is treated with bromobenzene, no phenyl thio-ether is formed (compare Bourgeois, Abstr., 1896, i, 17). The non-reactivity of the lead derivatives of dithiols with the bromo-derivatives of cyclic hydrocarbons is due, it is suggested, to the inclusion of the lead atom in a cyclic structure, thus: $S\genfrac{<}{>}{0pt}{}{C_6H_4\cdot S}{C_6H_4\cdot S}Pb$.

Sulphonedibenzenedi-p-*sulphonic chloride*, $SO_2(C_6H_4\cdot SO_2Cl)_2$, obtained by oxidation of the disulphonic chloride, dissolved in acetic acid, with potassium permanganate, crystallises from acetic acid in minute crystals, melts and decomposes at 217—220°, and is sparingly soluble in the usual solvents; when heated at 210° with phosphorus pentachloride it is converted into *p*-dichlorobenzene and thionyl chloride. The isomeride obtained by Otto and Rössing (Abstr., 1887, 263), which melts at 175—176° and is readily soluble in benzene, is probably the *meta*-compound.

Thiodibenzenedi-o-*sulphonic chloride* crystallises from ether or acetic acid in minute prisms and melts at 95—96° (the melting point is also given as 94—95° in the first paper). When oxidised by potassium permanganate, it is converted into the corresponding *sulphone*; this crystallises from benzene in minute prisms (perhaps containing benzene of crystallisation), melts at 80—90°, at the same time giving off benzene, then solidifies and re-melts at 147—148°. On exposure to air, the prismatic crystals become opaque and finally disintegrate. When heated at 210° with phosphorus pentachloride, it is converted first into *o*-chlorobenzenesulphonic chloride and *o*-benzenedisulphonic chloride and eventually into *o*-dichlorobenzene and thionyl chloride. T. A. H.

Aromatic Disulphinic Acids. JULIUS TRÖGER and WILHELM MEINE (*J. pr. Chem.*, 1903, [ii], 68, 313—340. Compare Otto and Casanova, Abstr., 1888, 255; Autenrieth and Hennings, Abstr., 1902, i, 390).—The aromatic disulphinic acids are more easily soluble in

water, less soluble in ether, and have less tendency to crystallise than the monosulphinic acids.

Zinc benzene-*m*-disulphinate, $C_6H_4(SO_2)_2Zn,3H_2O$, formed by the action of zinc dust on *m*-benzenedisulphonic chloride, crystallises from water (Pauly, *Ber.*, 1876, 9, 1595).

Whilst the action of chlorine or bromine on potassium benzene-*m*-disulphinate in aqueous solution leads to the formation of benzene-*m*-disulphonic chloride and bromide respectively, the action of iodine in aqueous potassium iodide or alcoholic solution results in oxidation of the disulphinate to benzene-*m*-disulphonic acid.

Benzene-m-*disulphonic bromide*, $C_6H_4(SO_2Br)_2$, separates from ether in yellow crystals and melts at 52° (compare Abstr., 1891, 718; 1893, i, 276).

When heated with water at 150°, benzene-*m*-disulphinic acid yields benzene-*m*-disulphonic acid (Abstr., 1902, i, 599) and *phenylene-benzene*-m-*dithiosulphonate*, $C_6H_4(SO_2{\cdot}S)_2{:}C_6H_4$, which is a white, amorphous powder, insoluble in water. *Methyl benzene*-m-*disulphinate*, formed by the action of methyl chlorocarbonate on the potassium salt, is a viscid, yellow oil.

m-Phenylenebisalkylsulphones are obtained by the action of the alkyl haloid on potassium benzene-*m*-disulphinate.

m-*Phenylenebismethylsulphone*, $C_6H_4(SO_2Me)_2$, crystallises in white leaflets and melts at 195—196°. m-*Phenylenebispropylsulphone* crystallises in white needles and melts at 109—110°. m-*Phenylenebis*-n-*butylsulphone* is a yellow oil, is easily soluble in alcohol or ether, and insoluble in water. m-*Phenylenebisallylsulphone* crystallises in white leaflets and melts at 105°. m-*Phenylenebisdichloropropylsulphone*, $C_6H_4(SO_2{\cdot}C_3H_5Cl_2)_2$, formed by the action of chlorine on the diallylsulphone in chloroform solution, is a yellowish-brown, viscid mass. m-*Phenylenebisdibromopropylsulphone* is a yellow, viscid oil. m-*Phenylenebisbromopropylsulphone*, $C_6H_4(SO_2{\cdot}C_3H_6Br)_2$, crystallises in white leaflets and melts at 74°. *m*-Phenylenebisiodomethylsulphone is formed when methylene iodide and potassium benzene-*m*-disulphinate are heated together under atmospheric pressure, and melts at 248° (compare Autenrieth and Hennings, *loc. cit.*).

m-*Phenylenebisacetonylsulphone*, formed by warming chloroacetone with potassium benzene-*m*-disulphinate in alcoholic solution, crystallises in slightly yellow needles, melts at 150—151°, and forms a dioxime, $C_6H_4(SO_2{\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH)_2$, which crystallises in yellow, prismatic needles and melts at 198—199°. The action of phenylhydrazine on *m*-phenylenedi-acetonylsulphone leads to the formation of a *monophenylhydrazone*, $C_6H_4(SO_2{\cdot}CH_2{\cdot}COMe){\cdot}SO_2{\cdot}CH_2{\cdot}CMe{:}N_2HPh$, which crystallises in nodules and melts and decomposes at 152°, and a *diphenylhydrazone*, which separates from alcohol in glistening, yellow crystals and melts and decomposes at 172°.

Methyl m-*phenylenebis-sulphoneacetate*, $C_6H_4(SO_2{\cdot}CH_2{\cdot}CO_2Me)_2$, formed by the action of methyl chloroacetate on potassium benzene-*m*-disulphinate, separates from ethyl acetate in thick, white crystals and melts at 96—97°. The *ethyl* ester, formed by the action of ethyl chloroacetate, crystallises in white leaflets, melts at 86—87°, and, on hydrolysis with aqueous sodium hydroxide, yields m-*phenylenebis-sul-*

phoneacetic acid, which crystallises in white needles, and, when heated, decomposes with formation of phenylenedi-methylsulphone (?).

m-*Phenylenebis-sulphoneacetamide,* formed by the action of chloroacetamide on potassium benzene-*m*-disulphinate, crystallises in white needles, melts at 229—230°, and at higher temperatures loses ammonia with formation of the *imide. Ethyl* m-*phenylenebis-sulphonepropionate* is a yellow oil and, on hydrolysis, yields the *acid,* $C_6H_4(SO_2 \cdot CH_2 \cdot CO_2H)_2$, which is a colourless oil; the *barium* salt forms white crystals. *Ethyl* m-*phenylenebis-sulphonebutyrate* crystallises in white needles and melts at 96°; the *acid* is an oil; the *barium* salt crystallises in stellate aggregates of needles.

Potassium *m*-phenylenedi-thiosulphonate (Abstr., 1902, i, 599) is formed when potassium *m*-phenylenedisulphinate and sulphur are heated together; it crystallises from alcohol in long, white needles.

Benzene-*p*-disulphinic acid, which crystallises in small, white needles, is formed by the action of sulphuric acid on a concentrated aqueous solution of *potassium benzene* p-*disulphinate,* prepared by Schiller and Otto's method (this Journal, 1877, i, 312), from benzene-*p*-disulphonic chloride. The *barium* salt, $C_6H_4(SO_2)_2Ba$, is white.

p-Phenylenebismethylsulphone, formed by the action of methyl iodide on potassium benzene-*p*-disulphinate, crystallises in flat, white needles and melts at 255—256°.

Zinc toluene-2 : 4-*disulphinate,* prepared by the action of zinc dust on toluene-2 : 4-disulphonic chloride, crystallises in thin, white needles, and, with concentrated aqueous potassium carbonate solution, yields the *potassium* salt from which the acid is prepared. *Toluene*-2 :4-*disulphinic acid,* $C_7H_6(SO_2H)_2$, is an oil, is soluble in water, and in presence of moisture bleaches litmus paper; the *sodium* salt and the *barium* salt form white crystals. When heated with water, toluene-2 : 4-disulphinic acid yields toluene-2 : 4-disulphonic acid and *tolylene toluene*-2 : 4-*di-thiosulphonate,* $C_7H_6(SO_2 \cdot S)_2 : C_7H_6$, which is a white, amorphous powder insoluble in water. The action of chlorine on potassium toluene-2 : 4-disulphinate leads to the formation of toluene-2 : 4-disulphonic chloride; of bromine, to the formation of *toluene*-2 : 4-*disulphonic bromide,* which is a white solid and melts at 78°; and of iodine in potassium iodide solution, to oxidation to toluene-2 : 4-disulphonic acid.

Methyl toluene-2 : 4-*disulphinate,* formed by the action of methyl chlorocarbonate on the potassium salt, is a viscid, yellow oil.

Tolylene-2 : 4-*bismethylsulphone,* $C_7H_6(SO_2Me)_2$, crystallises in white leaflets and melts at 153—154°; the *bisethylsulphone* separates from ether sometimes in crystals, sometimes as an oil; the *bis*-n-*propylsulphone* separates from alcohol in right-angled crystals and melts at 83—84°; the *bisbutylsulphone* is a viscid, yellow oil; the *bisallylsulphone* crystallises in white leaflets and melts at 89—90°.

Tolylene-2 : 4-*bisacetonylsulphone* crystallises in yellowish-white, prismatic needles and melts at 127°. *Ethyl tolylene*-2 : 4-*bis-sulphoneacetate* is a viscid, yellow oil; the free *acid* is an oil; the *barium* salt is a white powder. *Tolylene*-2 : 4-*bis-sulphonacetamide* crystallises in white needles and melts and decomposes at 230°. *Ethyl tolylene*-2 : 4-*bis*-

sulphonebutyrate and the free *acid* are yellow oils; the *barium* salt crystallises in white leaflets.

Naphthalene-2 : 7-*disulphinic acid*, prepared from Ebert and Merz's naphthalenedisulphonic chloride (*Ber.*, 1876, 9, 597), is a solid, has bleaching properties like the other disulphinic acids. When heated with methyl iodide, the *potassium* salt yields *naphthalene*-2 : 7-*bismethylsulphone*, which is an amorphous substance. G. Y.

Triphenylmethyl Acetate. Moses Gomberg and G. T. Davis (*Ber.*, 1903, 36, 3924—3927. Compare Abstr., 1902, i, 534).—*Triphenylmethyl acetate*, $CPh_3 \cdot OAc$, prepared by the action of silver acetate on triphenylchloromethane in benzene or ether, crystallises from light petroleum or ethyl acetate, and melts at 87—88°. When dissolved in acetyl chloride, it is at once converted into triphenylchloromethane; as Allen and Kölliker (Abstr., 1885, 655) and Herzig and Wengraf (Abstr., 1901, i, 702) used acetyl chloride in preparing their so-called triphenylmethyl acetate, it is obvious that their substance could not have been the real acetate; it was probably triphenylchloromethane. The authors show that this substance only is formed by the interaction of acetyl chloride and triphenylcarbinol ethyl ether, and that triphenylcarbinol is not attacked by acetic anhydride. W. A. D.

Existence of a Class of Substances Analogous to Triphenylmethyl. Moses Gomberg (*Ber.*, 1903, 36, 3927—3930. Compare Abstr., 1902, i, 534, 600).—The action of silver, zinc, or mercury on tri-*p*-tolylchloromethane, phenyl-di-*p*-tolylchloromethane, tri-*p*-nitrotriphenylchloromethane, or tri-*p*-anisylchloromethane is similar to the action of the same metals on triphenylchloromethane; in every case, a colour is first imparted to the liquid, probably owing to the formation of a coloured radicle similar to triphenylmethyl. The colours vary with the different substances, and soon disappear owing to the oxidation of the product first formed to substances analogous to, but more complex than, triphenylmethyl peroxide. W. A. D.

Gradual Synthesis of the Benzene Ring. Maurice Delacre and Louis Gesché (*Bull. Acad. Roy. Belg.*, 1903, 735—756. Compare Abstr., 1902, i, 774).—The authors now find that the hydrocarbon, which they named dypnopinalcolene (Abstr., 1900, i, 603), and to which they ascribed the formula $C_{32}H_{26}$, is identical with the hydrocarbon, $C_{25}H_{22}$, obtained by the action of potassium hydroxide dissolved in alcohol on dypnone (Gesché, Abstr., 1901, i, 604). This melts at 98°, boils at 292—295° under 40 mm. pressure, and is soluble in alcohol, benzene, or acetic acid; from the latter, it separates in a mixture of leaflets and needles. When reduced by sodium amalgam, it is converted into a mixture of two isomeric *hydrocarbons*, $C_{25}H_{24}$, one of which crystallises from alcohol in silky needles, melts at 145°, boils at 275—280° under 27 mm. pressure, is soluble in ether (2·7 per cent.), boiling alcohol (1·5 per cent.), and cold alcohol (0·13 per cent.), and is partially converted by distillation under atmospheric pressure into its isomeride. The latter separates from alcohol in vitreous crystals and from light petroleum in large leaflets and melts at about 115°. It

dissolves in ether (3·7 per cent.), boiling alcohol (2·5 per cent.), and cold alcohol (0·22 per cent.), but these constants are probably influenced by the presence in the material employed of a small amount of the less fusible isomeride. When distilled under atmospheric pressure, it is partially converted into its isomeride. When the hydrocarbon, $C_{25}H_{22}$, is treated with bromine dissolved in carbon disulphide, it is converted into a *bromo*-derivative, $C_{25}H_{19}Br$; this forms large, transparent crystals, melts at 140°, boils at 360°, and is soluble in benzene and chloroform. It is not attacked by potassium hydroxide in alcohol, but is slowly reduced by sodium amalgam in presence of alcohol, forming a *substance* which crystallises in minute needles and melts at 88—89°.

The hydrocarbon, $C_{25}H_{22}$, and its reduction products, when reduced with hydriodic acid, furnish a mixture of two crystalline *hydrocarbons*, $C_{25}H_{26}$, and a small quantity of a *hydrocarbon* volatile in steam and possessing an odour like that of ethylbenzene.

On distillation, the hydrocarbon, $C_{25}H_{22}$, and its reduction products furnish triphenylbenzene and a mixture of volatile hydrocarbons (compare Abstr., 1900, i, 603). T. A. H.

Dibromosulphonaphthalic Acid. GUIDO BARGELLINI (*L'Orosi*, 1902, **25**, 289—293).—The acid containing sulphur and bromine, previously mentioned by Francesconi and the author (*Gazzetta*, 1902, **32**, ii, 78; Abstr., 1903, i, 34) is found to be a *dibromosulphonaphthalic acid*, $SO_3H{\cdot}C_{10}H_3Br_2(CO_2H)_2$, and is best prepared by heating naphthalic anhydride with fuming sulphuric acid at 70—80° for three hours, during which bromine is gradually added, the whole being then heated for an hour at 100° and for 4 hours at 200°. It crystallises in white needles melting at 204—205°, dissolves in water, ethyl acetate, methyl or ethyl alcohol or acetic acid, and, to a slight extent, in ether or benzene; it is soluble also in dilute aqueous solutions of alkali hydroxides or carbonates or ammonia. The composition of its *barium* salt ($+8H_2O$) shows the acid to be tribasic. The acid dissolves readily in concentrated sulphuric acid, giving a yellow solution exhibiting no fluorescence. When heated with resorcinol, in molecular proportion, in presence of zinc chloride, the acid gives the corresponding fluorescein, which dissolves in dilute sodium hydroxide solution giving a dark orange coloured solution, showing a green fluorescence less intense than that exhibited by the fluorescein of either naphthalic or bromonaphthalic anhydride; this alkaline solution dyes silk a brick-red colour. T. H. P.

Application of Pyridine in the Preparation of some Amide Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1903, **137**, 712—714).—Secondary and tertiary amides may be prepared by the action of acyl chlorides on amides and anilides in presence of pyridine. The reaction takes place readily with aromatic acyl chlorides; the temperature must be kept low when fatty chlorides are employed, on account of their action on pyridine.

Dibenzanilide melts at 164° when pure (compare Kay, Abstr., 1894,

i, 77). The supposed isomeride of lower melting point (Higgin, Trans., 1882, **41**, 132) is a mixture of the two benzoyl derivatives.

The following new compounds have been prepared: p-*toluoyl*-o-*hydrazotoluene*, melting at 132°, and reacting with benzoyl chloride to form *benzoyl*-p-*toluoyl*-o-*hydrazotoluene*, melting at 182°; *benzoyl*-p-*toluoylaniline*, melting at 159—160°; *benzoylbenzenesulphanilide*, melting at 114°; *dibenzenesulphanilide*, melting at 143—144°; iso*butyrylacetamide*, melting at 177—178°; and iso*butyrylacetanilide*, melting at 49—50°. C. H. D.

Action of Aromatic Amines on Ethylenedisulphonic Chloride. Derivatives of Vinylsulphonic Acid. WILHELM AUTENRIETH and JULIUS KOBURGER (*Ber.*, 1903, **36**, 3626—3634).—Aniline and ethylenedisulphonic chloride interact to form vinylsulphanilide and sulphur dioxide (Autenrieth and Rudolph, Abstr., 1902, i, 22). This reaction takes place only with $\alpha\beta$-disulphonic chlorides, and has now been extended in order to determine the influence of substitution in the amine employed on the course of the action. *o*-, *m*-, and *p*-Toluidines, *m*-nitroaniline, *m*-chloroaniline, and *p*-phenetidine behave towards ethylenedisulphonic chloride like aniline; *o*-, *m*-, and *p*-toluidines react with equal readiness to give quantitative yields of the corresponding vinylsulphontoluidides, but *m*-nitroaniline, owing to its positive nitro-group, does not readily react, whilst the weak base, *o*-nitroaniline, does not react at all.

The vinylsulphonanilides prepared are acid in character, being readily soluble in aqueous solutions of alkalis, from which they are reprecipitated on the addition of acid. They are readily alkylated and acetylated, but cannot be benzoylated.

Vinylsulphon-p-*toluidide*, $CH_2\!:\!CH\cdot SO_2\cdot NH\cdot C_6H_4Me$, prepared by the action of *p*-toluidine on ethylenedisulphonic chloride in benzene solution, separates from dilute alcohol in glistening, white leaflets and melts at 74°. Its *acetyl* derivative crystallises from dilute alcohol in glistening leaflets and melts at 87°.

Vinylsulphon-o-*toluidide* separates from dilute alcohol in leaflets and melts at 64—65°. Its *acetyl* derivative separates from dilute alcohol in fine prisms and melts at 69°.

Vinylsulphon-m-*toluidide* separates from dilute alcohol in prisms and melts at 88°.

Vinylsulphon-m-*nitroanilide*, $CH_2\!:\!CH\cdot SO_2\cdot NH\cdot C_6H_4\cdot NO_2$, prepared by boiling a concentrated benzene solution of *m*-nitroaniline and ethylenedisulphonic chloride for 1 hour, separates from dilute alcohol in yellow prisms and melts at 119°.

Vinylsulphon-p-*phenetidide*, $CH_2\!:\!CH\cdot SO_2\cdot NH\cdot C_6H_4\cdot OEt$, separates from water or dilute alcohol in glistening, white leaflets and melts at 88°. Its *acetyl* derivative forms slender prisms and melts at 70°.

Vinylsulphon-o-*nitro*-p-*phenetidide*, prepared by nitrating vinylsulphon-*p*-phenetidide, forms yellow prisms and melts at 92°. When reduced by zinc dust, it forms *m*-ethoxy-*o*-phenylenediamine, which condenses with benzil to form *m*-ethoxydiphenylquinoxaline.

When excess of bromine acts on vinylsulphonanilide, tribromoaniline and the additive compound, $CH_2Br\cdot CHBr\cdot SO_2\cdot NHPh$, are formed

(compare Autenrieth and Rudolph, *loc. cit.*). This action proceeds in two stages, firstly, the simple addition of bromine to the sulphonanilide, and secondly, the decomposition of the latter additive compound with evolution of hydrogen bromide. With vinylsulphon-*p*-phenetidide, the main action consists in the addition of bromine. *Dibromoethylsulphon*-p-*phenetidide*, $CH_2Br\cdot CHBr\cdot SO_2\cdot NH\cdot C_6H_4\cdot OEt$, separates from dilute alcohol in colourless, glistening prisms and melts at 139°; when hydrolysed by concentrated hydrochloric acid, it forms *p*-phenetidine and not a dibromophenetidine, thus showing that the bromine has not been substituted in the benzene ring. A. McK.

Condensation of Mercaptans with Nitriles. WILHELM AUTENRIETH and A. BRÜNING (*Ber.*, 1903, 36, 3464—3469).—*Benziminothiophenyl ether*, $NH\colon CPh\cdot SPh$, prepared by condensing benzonitrile and thiophenol with dry hydrogen chloride, separates from ether in well-formed prisms and melts at 48°; the *hydrochloride* melts and decomposes at 178°, liberating hydrogen chloride, and dissolves unchanged in cold water, but is completely decomposed on boiling the solution.

Acetiminothiophenyl ether, $NH\colon CMe\cdot SPh$, was obtained as an unstable syrup; the *hydrochloride* melts and decomposes at 120°.

Propioniminothiophenyl ether, $NH\colon CEt\cdot SPh$, was only isolated as the *hydrochloride*, which is soluble in water, but begins to decompose at once.

Phenylacetiminothiophenyl ether, $NH\colon C(CH_2Ph)\cdot SPh$, separates in white needles, but soon decomposes into its constituents; the *hydrochloride* separates in white crystals and melts at 158°.

The *hydrochloride* of *succiniminothiophenyl ether*, $C_2H_4[C(\colon NH)\cdot SPh]_2$, melts at 145° and is slowly decomposed by cold water.

Succiniminodithioethylene ether, $\begin{matrix} CH_2\cdot C(NH)\cdot S\cdot CH_2 \\ | \qquad\qquad\qquad | \\ CH_2\cdot C(NH)\cdot S\cdot CH_2 \end{matrix}$, was obtained as a yellow syrup, which gradually solidified; the mono-*hydrochloride*, $C_6H_{11}N_2S_2Cl$, is an amorphous, dark green powder, soluble in water, which dyes silk and wool, but the aqueous solution soon deposits yellow flocks, and the dyed fabric, although stable to light, is turned yellow by alkalis.

Formiminothiophenyl ether, $NH\colon CH\cdot SPh$, was only isolated as its *hydrochloride*, which is very soluble in water but soon decomposes.

T. M. L

***p*-Nitroaminodiphenylamine.** HEINRICH SCHOTT (D.R.-P. 145061).—*p*-Dinitrodiphenylamine may be reduced by warming with a solution of sodium sulphide, with or without the addition of sodium hydroxide or sulphur, forming *p*-nitro-*p*-aminodiphenylamine, a brown, crystalline powder, dissolving in alcohol or dilute hydrochloric acid and forming a soluble diazonium compound. *p*-Dinitrodiphenylnitrosoamine may be reduced in the same manner. The *p*-nitro-*o*-amino-compound, a small quantity of which is produced at the same time, is not diazotisable, and the reduction product may therefore be employed directly in the preparation of azo-dyes. C. H. D.

Reduction of 2 : 5-Dimethylbenzaldazine and the Preparation of some Salts [of 2 : 5-Dimethyldibenzylamine]. EVERHART PERCY HARDING and LILLIAN COHEN (*J. Amer. Chem. Soc.*, 1903, **25**, 1091—1093).—When 2 : 5-dimethylbenzaldazine is reduced with zinc dust and acetic acid, dimethyldibenzylamine is produced. The *hydrochloride, picrate, mercurichloride*, and *platinichloride* are described.

E. G.

Existence of Miller and Plöchl's Stereoisomeric Anils. ALEXANDER EIBNER (*Annalen*, 1903, **329**, 210—224. Compare Abstr., 1901, i, 640).—[With M. AMANN.]—In order to ascertain whether the anhydro-compound obtained from propaldehyde and aniline (Sender's base) was a di-secondary base analogous to the anhydro-bases previously investigated (*loc. cit.*) or a secondary-tertiary base, a series of reactions have been studied.

The base could not be reduced by sodium and amyl alcohol, and is accordingly neither a di-secondary or a secondary-tertiary base, but more probably contains an azomethine group, $H\cdot C{:}N\cdot$.

The *benzoyl* derivative of Sender's base, $C_{19}H_{21}N_2Bz$, forms large, cubic crystals with 1 mol. of alcohol, which belong to the rhombohedric system [$a : c = 1 : 0.3670$]; when free from alcohol, it melts at 144° and is remarkably stable, resisting three hours' boiling with concentrated acids. Unlike Eckstein's base (*loc. cit.*), it does not yield a nitrosoamine, a fact which shows that an anilino-group is no longer present. Since the azomethine group is able to form additive products, it is probable that benzoyl chloride is first added on, and then a ring produced with the elimination of hydrogen chloride, thus:

$$\begin{array}{l} CHMe\cdot CH\cdot NPhBz \\ \;| \qquad\quad | \\ CHEt-NPh \end{array}.$$

When propylideneaniline is treated with hydrogen chloride in ethereal solution, an unstable *dihydrochloride*, $C_{16}H_{22}N,2HCl$, is produced, which loses hydrogen chloride, becoming converted into a *hydrochloride*, $C_{16}H_{22}N,HCl$; this behaviour indicates the presence of an azomethine group.

Since bromine forms, with the azomethine group of benzylideneaniline, an unstable additive product, which decomposes, yielding *p*-bromoaniline and benzaldehyde, it was probable that a similar behaviour would be observed in the case of this base; no additive product was isolated, but 2 : 6-dibromoaniline and other brominated anilines were formed.

With nitrous acid, a very unstable nitrosoamine is formed; in the absence of water, when nitrous fumes, dried by phosphoric oxide, are passed into a chloroform solution of the base, benzenediazonium nitrate is formed. With benzylideneaniline, a similar decomposition takes place, but in this case benzylideneaminoazobenzene is also produced. Neither the dinitrosoamines of Eckstein's nor Eibner's base showed this tendency to decompose with the formation of diazonium salts. On investigating the *dinitrosoamine* of the base obtained from acetaldehyde and *p*-toluidine, $C_{18}H_{20}O_2N_4$ (which crystallises in pale yellow needles melting at 165°), and the *dinitrosoamine* of the base prepared from acetaldehyde and *as*-*m*-xylidine, $C_{20}H_{24}O_2N_4$ (which

forms yellow needles melting at 79—80°), it was found that in neither case was diazonium salts formed. Both these bases are accordingly compounds of the type NHAr·CHMe·CH:CH·NHAr, whereas Sender's base is represented by the formula NHPh·CHEt·CHMe·CH:NPh.

K. J. P. O.

Problem of Activity in connection with Asymmetric Nitrogen. EDGAR WEDEKIND (*Zeit. physikal. Chem*, 1903, 45, 235—248. Compare Abstr., 1899, i, 351; 1900, i, 155).—The author has determined the most favourable conditions for the resolution of *a*-phenylbenzylmethylallylammonium iodide into its active constituents with the aid of *d*-camphorsulphonic acid (see Pope and Peachey, Trans., 1899, 75, 1127; Pope and Harvey, Trans., 1901, 79, 828). The same lines have been followed in an attempt to resolve *p*-tolylbenzylmethylallylammonium iodide and *p*-tolylmethylethylallylammonium iodide, but without success in either case.

Pope and Harvey observed (p. 831, *loc. cit.*) that a freshly prepared chloroform solution of active phenylbenzylmethylallylammonium iodide gradually became inactive, and they attributed this to a dissociation into benzyl iodide and methylallylaniline. Boiling point determinations, with chloroform as solvent, have been made to further elucidate this point, and the molecular weight found is less than one-third of the normal value. Similar experiments with *p*-tolylmethylethylallylammonium iodide gave a molecular weight more than half the normal value.

As shown previously by the author (Abstr., 1900, i, 155), benzylphenylmethylallylammonium salts undergo hydrolysis when their aqueous solutions are heated. By measuring the conductivity of phenylbenzylmethylallylammonium, *p*-tolylbenzylmethylallylammonium, and *p*-tolylmethylethylallylammonium *d*-camphorsulphonates in aqueous solution before and after heating, an idea of the relative stability of these substances may be obtained, for the acid liberated by hydrolysis (if such takes place) causes a marked increase in the conductivity. It has thus been found that the *p*-tolylbenzylmethylallylammonium salt is more stable than the phenylbenzylmethylallylammonium salt, whilst the *p*-tolylmethylethylallylammonium salt is hydrolysed only to a very slight extent. It is all the more remarkable that this salt has not been obtained in the active form.

It is noted, finally, that the resolution of phenylbenzylmethylallylammonium salt can be effected only with the aid of *d*-camphorsulphonic acid; the other methods usually employed are ineffective. J. C. P.

Phenylmethylethylallylammonium Iodide. EDGAR WEDEKIND (*Ber.*, 1903, 36, 3791—3796).—As the preparation of the halogen salts of phenylbenzylmethylallylammonium in three different ways (Abstr., 1899, i, 351; 1900, i, 155) had shown that it exists in two different isomeric modifications, the same methods have been applied to the preparation of a lower homologue. A mixture of methylethylaniline and allyl iodide soon solidifies to a crystalline mass; recrystallised from chloroform, *phenylmethylethylallylammonium iodide* forms glistening plates belonging to the rhombic system [$a:b:c=$

0·9115 : 1 : 0·7208], containing a molecule of the solvent and melting indistinctly at 75—80°. The well-characterised *platinichloride* crystallises from boiling water in long, reddish-yellow needles melting just above 182°.

Ethylallylaniline and methyl iodide unite to an amorphous substance different from that just described, but converted into it on treatment with chloroform; it forms an identical platinichloride. Methylallylaniline and ethyl iodide unite to give an exactly similar, amorphous compound. The corresponding bromide forms colourless crystals, isomorphous with the iodide, which decompose at 140°.

E. F. A.

Nitric Oxide and Grignard's Reagent. JULIUS SAND and FRITZ SINGER (*Annalen*, 1903, 329, 190—194. Compare Abstr., 1902, i, 851).—Although both uranyl chloride, UO_2Cl_2, and chromyl chloride react readily with magnesium alkyl haloids, the compounds produced are unstable and decomposed by water.

Nitric oxide forms an additive product with magnesium phenyl bromide, and appears to act as if it were dimolecular, N_2O_2; thus, $N_2O_2 + MgPhBr \rightarrow ON{\cdot}NPh{\cdot}O{\cdot}MgBr \rightarrow ON{\cdot}NPh{\cdot}OH$. Bromobenzene was allowed to interact with magnesium powder in the presence of ether, and pure nitric oxide led in after the air had been displaced from the vessel by means of hydrogen; the product was poured on to ice and the solution extracted with ether. The β-phenylnitrosohydroxylamine thus obtained melted at 59° and was identical with the nitrosoamine prepared by Bamberger (Abstr., 1894, i, 412); at the same time, a small quantity of diphenyl was isolated from the product of the reaction.

Nitrosomethylhydroxylamine was obtained in the form of its copper salt by the interaction of magnesium methiodide and nitric oxide; after the primary product of the reaction had been poured on to ice, copper oxide was added and the blue solution evaporated; the *copper* salt $(N_2Me_2O_2)_2Cu,\frac{1}{2}H_2O$, which is soluble in water and benzene, crystallises from aqueous alcohol in long, azure-blue needles

K. J. P. O.

Carbamide Oximes. JULIUS VON BRAUN and RUDOLF SCHWARZ (*Ber.*, 1903, 36, 3660—3663).—The cyanogen group in cyanoamides has the same additive power as the same group in nitriles, since cyanoamides form amides, thioamides, iminoethers, and amidines. The behaviour of cyanoamides towards hydroxylamine has now been studied.

Mono-substituted cyanoamides react with hydroxylamine very vigorously, but no definite compounds were isolated as products of the action. Disubstituted cyanoamides unite with hydroxylamine in molecular proportions.

Phenylmethylcyanoamide in methyl alcoholic solution unites with hydroxylamine to form the *oxime*, $NMePh{\cdot}CN,NH_2{\cdot}OH$, which melts at 102°; it is a weak base and crystallises unchanged from its solution in aqueous hydrochloric or sulphuric acid. Its *hydrochloride*, prepared by passing hydrogen chloride into its ethereal alcoholic solution,

forms a snow-white powder and melts at 189°; its *picrate* melts at 120—121°.

Dipropylcyanoamide unites with hydroxylamine to form the *oxime*, $NPr_2^{\alpha}\cdot CN,NH_2\cdot OH$, which melts at 115°; the *picrate* of the latter melts at 185°.

Diphenylcyanoamide in a similar manner forms the *oxime*, $NPh_2\cdot CN,NH_2\cdot OH$, which melts at 161°; its *hydrochloride* melts at 169—170°, whilst its *picrate* softens at 165° and melts completely at 182°.

These oximes are most probably carbamide derivatives of the type $NR_2\cdot C(:N\cdot OH)\cdot NH_2$. A. McK.

The Beckmann Rearrangement. III. Stereoisomeric Chloroimino-acid Ethers. JULIUS STIEGLITZ and RICHARD B. EARLE (*Amer. Chem. J.*, 1903, 30, 399—412. Compare Abstr., 1897, i, 43, and 1903, i, 235).—m-*Nitrobenzoylchloroamide*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NHCl,$$

obtained by the action of sodium hypochlorite on nitrobenzamide, crystallises from a mixture of acetone and benzene and melts at 183—184°. When this compound is treated with diazomethane, the α-modification of *methyl chloroimino*-m-*nitrobenzoate*,

$$NO_2\cdot C_6H_4\cdot C(OMe):NCl,$$

is produced, which crystallises in long prisms or rectangular plates, melts at 86·5—87·5°, and is readily soluble in chloroform, benzene, or acetone; by the action of hydrogen chloride, it is converted into the hydrochloride of methyl imino-*m*-nitrobenzoate.

When the hydrochloride of methyl imino-*m*-nitrobenzoate is added to a large excess of sodium hypochlorite at 30°, a product is obtained consisting of a mixture of the α- and β-modifications of methyl chloroimino-*m*-nitrobenzoate, which may be separated by repeated crystallisation from a mixture of chloroform and light petroleum. The β-*modification* crystallises in thin, rhombohedric plates, melts at 81—82°, and by the action of dry hydrogen chloride is converted into methyl iminonitrobenzoate.

The molecular weight of each modification was determined by the cryoscopic method and found to agree with that required by the formula $NO_2\cdot C_6H_4\cdot C(OMe):NCl$. Both isomerides are stable compounds and remain unchanged when heated for some time at 80°, or even for a few minutes at 140°. The change of one isomeride into the other has never been observed. Physical and structural isomerism being excluded, it follows that the compounds must be stereoisomerides, one being the *syn*-modification, $\begin{array}{c}NO_2\cdot C_6H_4\cdot C\cdot OMe\\ \quad\quad\quad\;\; \| \\ \quad\quad\quad Cl\cdot N\end{array}$, and the other the *anti*-modification, $\begin{array}{c}NO_2\cdot C_6H_4\cdot C\cdot OMe\\ \quad\quad\quad\;\; \| \\ \quad\quad\quad\;\; N\cdot Cl\end{array}$.

m-*Nitrobenzoylmethylchloroamide*, $NO_2\cdot C_6H_4\cdot CO\cdot NClMe$, prepared by the action of chlorine on *m*-nitrobenzoylmethylamide, crystallises in thick, monoclinic prisms, melts at 76—77°, and when treated with dry hydrogen chloride is reconverted into *m*-nitrobenzoylmethylamide.

E. G.

The Beckmann Rearrangement. IV. The Formation of Acylalkylcarbamides in Hofmann's Reaction. Julius Stieglitz and Richard B. Earle (*Amer. Chem. J.*, 1903, 30, 412—421).—It is found that, both in the aliphatic and aromatic series, acid chloroamides condense very readily with carbimides with formation of acylalkylcarbamides, whereas the acid amides do not respond at all to the action of carbimides. The formation of acylalkylcarbamides in Hofmann's reaction is therefore due to the ready condensation of a carbimide, the primary product of the rearrangement of a molecule of an acid halogen-amide, with a second molecule of the latter, and to a subsequent hydrolysis of the condensation product. The action is thus in harmony with the conception that a carbimide may always be considered to be the first product of the "Beckmann rearrangement" of an acid halogen-amide.

By the action of *p*-chlorophenylcarbimide on benzoylchloroamide, s-*benzoyl*-p-*chlorophenylcarbamide*, $C_6H_4Cl·NH·CO·NHBz$, is obtained, which crystallises in white needles and melts at 235—237°. The same compound may be prepared by the action of *p*-chlorophenylcarbimide on benzamide and by the action of benzoyl chloride on *p*-chlorophenylcarbamide.

When a solution of phenylcarbimide in dry benzene is warmed with dry benzoylchloroamide, benzoyl-*p*-chlorophenylcarbamide is formed, the chlorine atom having migrated into the benzene nucleus. In the presence of alkali, phenylcarbimide reacts with benzoylchloroamide with formation of *s*-benzoylphenylcarbamide; this compound is also produced under the same conditions by the action of phenylcarbimide on benzoylbromoamide.

By the action of phenylcarbimide on acetylchloroamide, *s*-acetylphenylcarbamide is formed. Acetamide does not react with phenylcarbimide. Methylcarbimide reacts with acetylchloroamide with formation of *s*-acetylmethylcarbamide, but does not combine with acetamide.

Dibenzoylchloroamide, NBz_2Cl, obtained by the action of chlorine on the silver salt of dibenzamide, crystallises in white needles and melts at 86°. When heated, it shows no tendency to undergo a "Beckmann rearrangement," but is decomposed with formation of chlorine, benzonitrile, and benzoyl chloride. E. G.

***cyclo*Hexanol.** Arnold F. Holleman (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 201—203).—*cyclo*Hexanol, prepared by passing dry hydrogen through phenol heated at 160—170°, and then leading the resulting vaporous mixture over freshly reduced nickel at 140—160°, is a syrupy liquid and boils at 160—161°. It is oxidised by chromic acid to ketohexamethylene. A. McK.

Action of Oxygen on Magnesium Organo-haloid Compounds. Louis Bouveault (*Bull. Soc. chim.*, 1903, [iii], 29, 1051—1054. Compare Grignard, Abstr., 1900, i, 382; 1901, i, 679; and Zelinsky, 1902, i, 675).—When *cyclo*hexane is converted by Grignard's method (*loc. cit.*) into *cyclo*hexanecarboxylic acid (hexahydrobenzoic acid), about 20 per cent. of *cyclo*hexanol (hexahydrophenol) is simultane-

ously produced, which, it is suggested, is formed by the action of atmospheric oxygen on the magnesium compound of the haloid derivative of *cyclo*hexane employed (compare Bodroux, Abstr., 1903, i, 249, and Taboury, *ibid.*, 748). The validity of this hypothesis was confirmed by the conversion of magnesium-benzyl chloride into benzyl alcohol by the action of oxygen. T. A. H.

Action of Bromine and Chlorine on Phenols. Action of Bromine on *iso*Eugenol (3-Methoxy-*p*-propylenephenol). Theodor Zincke and O. Hahn (*Annalen*, 1903, 329, 1—36).—The products of the action of bromine on *iso*eugenol are analogous to the substances obtained from *p*-vinylphenol (Abstr., 1902, i, 615). Some of the derivatives of *iso*eugenol described in this paper have been previously prepared by Chasanowitz and Hell (Abstr., 1885, 779), Hell and Portman (Abstr., 1895, i, 657), and Auwers and Müller (Abstr., 1902, i, 212).

*iso*Eugenol dibromide (ψ-3-methoxy-4-$\alpha\beta$-dibromopropylphenol), prepared by adding an ethereal solution of bromine to an ethereal solution of *iso*eugenol, crystallises from benzene in large leaflets melting at 95° (Hell and Portman record 86—87°, and Auwers and Müller, 94—95°). On adding a few drops of sulphuric acid to its solution in acetic anhydride, the acetyl derivative (m. p. 125—126°) is formed. By the action of sodium carbonate on the ethereal solution of the dibromide, 2-*methoxy*-4-β-*bromopropylidenequinone*,

$$\mathrm{CHMeBr{\cdot}CH{:}C}{<}\begin{matrix}\mathrm{CH{=\!=}CH}\\\mathrm{CH{:}C(OMe)}\end{matrix}{>}\mathrm{CO},$$

is formed as a yellow oil.

2-Bromo*iso*eugenol dibromide (ψ-2-methoxy-6-bromo-4-$\alpha\beta$-dibromopropylphenol), prepared by brominating *iso*eugenol in ethereal solution, crystallises in needles melting at 138° (Auwers and Müller give 132—133°). 2-*Methoxy*-6-*bromo*-4-β-*bromopropylidenequinone*,

$$\mathrm{CHMeBr{\cdot}CH{:}C}{<}\begin{matrix}\mathrm{CH{=\!=}CBr}\\\mathrm{CH{:}C(OMe)}\end{matrix}{>}\mathrm{CO},$$

is prepared by treating an ethereal solution of the dibromide last mentioned with 10 per cent. aqueous sodium acetate; the ethereal solution assumes an intense yellow coloration and deposits the yellow prisms of the quinone, which sinters at 140° and decomposes at a higher temperature. The solutions in methyl or ethyl alcohol or acetic acid soon become colourless, whilst those in indifferent solvents become deep red. Under these conditions, probably polymeric quinones are formed. The quinone combines with hydrogen chloride and bromide producing ψ-chlorides and ψ-bromides; the ψ-chloride,

$$\mathrm{CHMeBr{\cdot}CHCl{\cdot}CH}{<}\begin{matrix}\mathrm{CH{=\!=}CBr}\\\mathrm{CH{=}C(OMe)}\end{matrix}{>}\mathrm{CO}\ \text{or}$$

$$\mathrm{CHMeBr{\cdot}CHCl{\cdot}C}{\lessdot}\begin{matrix}\mathrm{CH{=\!=}CBr}\\\mathrm{CH{\cdot}C(OMe)}\end{matrix}{\gtrdot}\mathrm{C{\cdot}OH},$$

is prepared by digesting the quinone with an acetic acid solution of hydrogen chloride; it crystallises in colourless needles melting at 110° and is insoluble in alkali hydroxides.

6-*Bromo*iso*eugenol* is obtained when the bromo*iso*eugenol dibromide or the quinone prepared from it, is reduced by hydriodic acid; it

forms a soluble white powder which sinters on heating. Its *acetyl* derivative is an amorphous powder.

On dissolving the quinone above mentioned in methyl alcohol, 2-*methoxy*-6-*bromo*-4-*α*-*methoxy*-*β*-*bromopropylphenol* is produced; it forms small, white needles, melting at 106—107° (Auwers, 104—105°), and is easily soluble in alkali hydroxides and carbonates. The corresponding ethoxypropyl compound crystallises in small, rhombic leaflets melting at 66—67° (Auwers, 78—80°). The corresponding hydroxy-compound, 2-methoxy-6-bromo-4-*α*-hydroxy-*β*-bromopropylphenol, is formed whenever the quinone is exposed to moisture, even moist air; it forms colourless needles melting at 144° (Auwers, 135—136°); the *diacetyl* derivative forms small crystals melting at 112—114°.

2-*Methoxy*-6-*bromo*-4-*α*-*acetoxy*-*β*-*bromopropylphenol* is formed when the corresponding bromo-compound just mentioned is heated with sodium acetate in acetic acid solution, or when the quinone is shaken with acetic acid; it forms rhombic crystals melting at 85—86° and is decomposed by alkali hydroxides.

The *acetyl* derivative of 6-bromo*iso*eugenol dibromide is produced when the dibromide is boiled for a short time with acetic anhydride, or when 2-methoxy-6-bromo-4-*α*-hydroxy-*β*-bromopropylphenol is heated with acetyl bromide, or finally by brominating *iso*eugenol acetate; it melts at 130—131°. The *acetyl* derivative of 6-bromo-4-*α*-chloro-*β*-bromopropylphenol, prepared by the action of acetyl chloride on the hydroxybromopropylphenol, crystallises in needles melting at 111—112°.

3 : 6-*Dibromo*iso*eugenol dibromide* (2-*methoxy*-3 : 6-*dibromo*-4-*αβ*-*dibromopropylphenol*), $CHMeBr\cdot CHBr\cdot CH<\substack{CBr:C(OMe)\\ CH=\!=\!=CBr}>CO$ or

$CHMeBr\cdot CHBr\cdot C\leqslant\substack{CBr:C(OMe)\\ CH\text{———}CBr}\geqslant C\cdot OH$, is easily prepared by treating the tribromo*iso*eugenol with bromine, and forms large, lustrous crystals melting at 124° and behaves as a *ψ*-bromide. On treatment with 10 per cent. aqueous sodium acetate, it is converted into 2-*methoxy*-3 : 6-*dibromo*-4-*β*-*bromopropylidenequinone*,

$CHMeBr\cdot CH:C<\substack{CBr:C(OMe)\\ CH=\!=\!=CBr}>CO$, which crystallises in yellow plates, begins to decompose at 175°, and melts at 200°; when dissolved in acetone, it is immediately converted into a white, amorphous substance, $C_{10}H_9O_2Br_3$, which is probably a polymeride.

3 : 6-*Dibromo*iso*eugenol*, $C_3H_5\cdot C_6HBr_2(OMe)\cdot OH$, is readily prepared by reducing the tetrabromo-compound by zinc and hydrobromic acid in ethereal solution; it crystallises in long, colourless needles melting at 102°, soluble in sodium hydroxide, and combining with bromine directly to form the tetrabromo-*ψ*-bromide just described. The *acetyl* derivative forms crystals melting at 123°.

2-*Methoxy*-3 : 6-*dibromo*-4-*α*-*methoxy*-*β*-*bromopropylphenol* is obtained from the tetrabromo-*ψ*-bromide or from the corresponding quinone by treatment with methyl alcohol; it forms small crystals melting at 111—112°, and is soluble in alkali hydroxides. 2-*Methoxy*-3 : 6-*dibromo*-4-*α*-*hydroxy*-*β*-*bromopropylphenol*, prepared in the same manner

as the hydroxy-compounds of similar constitution above described, forms cubic or octahedric crystals melting at 127—128°; the *diacetyl* derivative forms lustrous crystals melting at 139—140°. The corresponding *mono-acetyl* derivative, prepared by the action of acetic acid on the tetrabromo-ψ-bromide or on tribromopropylidenequinone, crystallises in colourless needles melting at 114—115°, and is converted by alkalis into an amorphous substance probably a quinone, and by acetic anhydride into the diacetyl derivative just described. On boiling the tetrabromo-ψ-bromide with acetic anhydride or on heating 3 : 6-dibromo*iso*eugenol dibromide under pressure at 100° with acetyl bromide, the *acetyl* derivative of the compound last mentioned is formed; it crystallises in colourless needles melting at 117—118°. The *acetyl* derivative of 3 : 6-dibromo-4-α-chloro-β-bromopropylphenol, prepared by the action of acetyl chloride on the dibromohydroxybromopropylphenol, crystallises in slender needles melting at 97—98°.

3 : 5 : 6-*Tribromo*iso*eugenol dibromide* (2-*methoxy*-3 : 5 : 6-*tribromo*-4-*aβ-dibromopropylphenol*), $CHBrMe{\cdot}CHBr{\cdot}CH{<}^{CBr:C(OMe)}_{CBr{=\!=}CBr}{>}CO$ or $CHBrMe{\cdot}CHBr{\cdot}C{<}^{CBr:C(OMe)}_{CBr{-\!-}CBr}{>}C{\cdot}OH$, is prepared by heating mol. proportions of dibromo*iso*eugenol dibromide and bromine under pressure at 100°, and crystallises from benzene in needles melting at 130°.

2-*Methoxy*-3 : 5 : 6-*tribromo*-4-*β-bromopropylidenequinone*, prepared from the compound last mentioned by the action of sodium acetate when the conditions are carefully regulated, crystallises in yellow needles decomposing when heated. With hydrogen chloride and bromide, it forms colourless, additive products; the *compound* with hydrogen chloride, which is prepared by passing the dry gas into a suspension of the quinone in ether, forms cubic crystals melting at 102—103° and is insoluble in alkalis.

On reducing the pentabromo-ψ-bromide with hydrogen iodide in acetic acid solution, 3 : 5 : 6-*tribromo*iso*eugenol* is formed; it crystallises in silky needles melting at 118°, and readily forms additive compounds with bromine, hydrogen bromide, &c. When the pentabromo-ψ-bromide or the corresponding propylidenequinone is warmed with methyl alcohol, 2-*methoxy*-3 : 5 : 6-*tribromo*-4-*α-methoxy-β-bromopropylphenol* is obtained as a colourless, crystalline substance melting at 126—127°. The corresponding *acetoxy*-derivative, prepared by substituting acetic acid for methyl alcohol, crystallises in long needles melting at 156—157°. The *acetyl* derivative of tribromo*iso*eugenol dibromide is easily prepared by treating the pentabromo-ψ-bromide with acetic anhydride and then adding a few drops of sulphuric acid; it crystallises in needles melting at 175°. K. J. P. O.

Interdependence of Acidity and Structure of Polycyclic Phenols. PAUL N. RAIKOW (*Chem. Zeit.*, 1903, 27, 1125—1127. Compare Abstr., 1903, i, 754).—The action of potassium hydroxide, potassium carbonate, potassium phosphate, ammonia, &c., on α-naphthol, β-naphthol, alizarin, purpurin, hexahydroxyanthraquinone, aurin, rosolic acid, phenolphthalein, fluorescein, eosin, iododeosin, tetraiodotetra-

chlorofluorescein, nitroso-β-naphthol, dinitro-α-naphthol, and tetranitro-dihydroxyanthraquinone was studied. The benzene ring, as a substituent in polycyclic phenols, exercises an acidifying influence, α-naphthol, for instance, being more acidic than phenol. In compounds with condensed benzene rings, the benzene ring substituent exerts a stronger acidifying influence the nearer it is to the hydroxyl grouping; thus α-naphthol is a stronger acid than β-naphthol. The further introduction of a hydroxyl grouping into a polycylic phenol increases the acidity, thus, purpurin is more strongly acidic than alizarin. Aurin and rosolic acid are more strongly acidic than phenolphthalein and fluorescein. A. McK.

4-Hydroxy-3-methyltriphenylcarbinol [Diphenyl-6-hydroxy-*m*-tolylcarbinol]. AUGUSTIN BISTRZYCKI and B. ZURBRIGGEN (*Ber.*, 1903, 36, 3558—3564).—4-*Hydroxy-3-methyltriphenylcarbinol* (α-form), $OH\cdot CPh_2\cdot C_6H_3Me\cdot OH$, prepared by dissolving 4-hydroxy-3-methyltriphenylacetic acid in concentrated sulphuric acid at the ordinary temperature, crystallises from dilute acetic acid in lustrous, yellow prisms, melts and decomposes at 107—108°, and gives a *potassium* salt, $C_{20}H_{17}O_2K$, which crystallises in colourless, glistening leaflets. The *acetyl* derivative, $OH\cdot CPh_2\cdot C_6H_3Me\cdot OAc$, crystallises from glacial acetic acid and melts at 127—128°. The m-*nitrobenzoyl* derivative, $OH\cdot CPh_2\cdot C_6H_3Me\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, prepared by the Lossen-Baumann method, crystallises from a mixture of benzene and light petroleum and melts at 118—119°. The *dimethyl ether*, $OMe\cdot CPh_2\cdot C_6H_3Me\cdot OMe$, prepared by passing hydrogen chloride through a solution of the carbinol in methyl alcohol, crystallises from methyl alcohol in microscopic plates and melts at 91—92°.

4-*Hydroxy* 3-*methyltriphenylmethane* [*Diphenyl*-6-*hydroxy*-m-*tolylmethane*], $CHPh_2\cdot C_6H_3Me\cdot OH$, prepared by reducing the corresponding carbinol with zinc and acetic acid, separates from dilute acetic acid in well-formed crystals and melts at 100°. The *acetyl* derivative forms colourless aggregates of prisms and melts at 63—64°; the m-*nitrobenzoyl* derivative crystallises from acetic acid in prismatic needles and melts at 93—94°. The *methyl ether*, $CHPh_2\cdot C_6H_3Me\cdot OMe$, crystallises from methyl alcohol in stellate aggregates of prisms and melts at 80—81°; the corresponding *ethyl ether* melts at 75°.

$\omega\omega$-*Diphenyl*-2-*methylquinomethane*, $CPh_2:C_6H_3Me:O$ (compare Auwers and Schröter, Abstr., 1903, i, 820), is formed when the foregoing carbinol is heated for 3—4 hours at 180°; it crystallises from benzene in microscopic plates and melts at 176°. W. A. D.

4-Hydroxy-3-methyltriphenylcarbinol [Diphenyl-6-hydroxy-*m*-tolylcarbinol] and *p*-Hydroxytriphenylcarbinol. AUGUSTIN BISTRZYCKI and CARL HERBST (*Ber.*, 1903, 36, 3565—3572. Compare preceding abstract and Abstr., 1901, i, 701; 1902, i, 776; Auwers and Schröter, Abstr., 1903, i, 820).—$\omega\omega$-Diphenyl-2-methylquinomethane, on reduction with zinc and acetic acid, is converted almost quantitatively into 4-hydroxy-3-methyltriphenylmethane, and when boiled with 50 per cent. acetic acid yields 4-hydroxy-3-methyltriphenyl-

carbinol; on boiling with alcoholic sodium ethoxide and decomposing the product with carbon dioxide, it gives *4-hydroxy-3-methyltriphenylcarbinyl ethyl ether*, $OEt\cdot CPh_2\cdot C_6H_3Me\cdot OH$, which crystallises from a mixture of benzene and light petroleum in colourless, four-sided plates and melts at 150—151°.

When ωω-diphenyl-2-methylquinomethane is boiled with alcoholic potassium hydroxide and the product precipitated by dilute acetic acid, a *substance* apparently isomeric and not identical with 4-hydroxy-3-methyltriphenylcarbinol is obtained; it crystallises from benzene in colourless needles or flat prisms, melts at 148—149°, and only differs from its isomeride in not losing water at 100°, whereas the carbinol melting at 107—108° begins to decompose at 50—60°, undergoing conversion into ωω-diphenyl-2-methylquinomethane. It is called provisionally the *β-form* of the carbinol, and can be reconverted into the α-form by simply warming with acetic acid; attempts to acetylate it gave only the acetyl derivative of the α-form. Auwers and Schröter (*loc. cit.*) have considered the two corresponding forms of *p*-hydroxytriphenylcarbinol to differ by $\frac{1}{2}H_2O$, but the authors consider them to have the formulæ $OH\cdot CPh_2\cdot CH{:}C_6H_3Me{:}O$ and

$$OH\cdot CPh_2\cdot C_6H_3Me\cdot OH.$$

The remainder of the paper is largely a reply to Auwers and Schröter's criticisms, but the following result is noteworthy. When *p*-ethoxytriphenylcarbinyl ethyl ether is boiled with acetic anhydride, acetic acid, or acetyl chloride, or heated alone at 150° for 4 hours, it is converted into *p*-ethoxytriphenylmethane. W. A. D.

Reduction of Unsaturated Phenol Ethers by Sodium and Alcohol. AUGUST KLAGES [with A. EPPELSHEIM] (*Ber.*, 1903, **36**, 3584—3597).—*2-Methoxy-1 α-hydroxyethylbenzene*,

$$OMe\cdot C_6H_4\cdot CHMe\cdot OH,$$

prepared by the action of magnesium methiodide on salicylaldehyde methyl ether, is a colourless, viscous liquid and boils at 119—120° under 11 mm. pressure. The *phenylurethane*, $C_{16}H_{17}O_3N$, crystallises from alcohol in colourless needles and melts at 106°.

o-Methoxyacetophenone, $OMe\cdot C_6H_4\cdot COMe$, boils at 120—121° under 13 mm. and at 239° under 757 mm. pressure. The *oxime*, $C_9H_{11}O_2N$, forms colourless needles and melts at 83°. The *phenylhydrazone*, $C_{15}H_{11}ON_2$, crystallises from alcohol in stout, colourless, glistening tablets and melts at 114°. The *semicarbazone*, $C_{10}H_{13}O_2N_3$, crystallises from alcohol in colourless needles and melts at 180—182°.

The chloride, $OMe\cdot C_6H_4\cdot CHMeCl$, was not purified but was converted into the *pyridinium chloride*, $C_5NH_5Cl\cdot CHMe\cdot C_6H_4\cdot OMe$, which separates from a mixture of alcohol and ether in colourless crystals and melts at 119—121°; the corresponding *picrate* separates from alcohol in small, yellow crystals and melts at 146—147°.

o-Vinylanisole, $OMe\cdot C_6H_4\cdot CH{:}CH_2$, prepared by heating the chloride with pyridine at 115°, is a mobile, refractive oil, with a phenol-like odour, boils at 82—83° under 11 mm. pressure, has a sp. gr. 1·0002 at 17°/4°, n_D 1·556, and is converted into a resin either when distilled under atmospheric pressure, or slowly at the ordinary temperature. It is reduced by sodium and alcohol to *o*-ethylanisole, which boils at 70—71°

under 11 mm. and at 186—188° under 758 mm. pressure, has a sp. gr. 0·9636 at 19°/4°, and n_D 1·512.

3-*Methoxy*-1-*a*-*hydroxyethylbenzene* is a colourless oil which boils at 132—133° under 12 mm. pressure, has a sp. gr. 1·0781 at 19°/4°, and n_D 1·5325 ; the *phenylurethane* was obtained only as an oil. *m*-Methoxyacetophenone, prepared by oxidising the carbinol, yields a *semicarbazone* which crystallises from acetic acid in minute, colourless needles and melts at 181—183°. m-*Vinylanisole* is a mobile liquid which boils at 89—90° under 14 mm. pressure, is oxidised by permanganate, and has a great tendency to polymerise. When reduced, it yields m-*ethylanisole*, a colourless liquid which boils at 77—78° under 12 mm. and at 196—197° under 758 mm. pressure, has a sp. gr. 0·95746 at 18°/4°, and n_D 1·5102.

4-*Methoxy*-1-*a*-*hydroxyethylbenzene*, $OMe\cdot C_6H_4\cdot CHMe\cdot OH$, is a colourless oil and has a sp. gr. 1·086 at 16°/4°, and n_D 1·537 ; the *phenylurethane*, separates from alcohol in colourless needles and melts at 82—83°. *p*-Vinylanisole is a mobile liquid which boils at 90—91° under 13 mm. and at 204—205° under 756 mm. pressure, and has a sp. gr. 1·0001 at 13°/4°, and n_D 1·5642 ; Perkin gives b. p. 203—204°, sp. gr. 1·0029 at 15°. It is reduced to p-*ethylanisole*, $OMe\cdot C_6H_4Et$, which boils at 79—80° under 13 mm. and at 195—197° under atmospheric pressure, and has a sp. gr. 0·9624 at 15°/4° and n_D 1·5094.

4-*Ethoxy*-1-*a*-*hydroxyethylbenzene*, $OEt\cdot C_6H_4\cdot CHMe\cdot OH$, distils at 140—142° under 11 mm. pressure, crystallises from light petroleum in needles, and melts at 48° ; the *phenylurethane*, $C_{17}H_{19}O_3N$, separates from alcohol in colourless flakes and melts at 81°. p-*Vinylphenetole*, $OEt\cdot C_6H_4\cdot CH{:}CH_2$, boils at 108—110° under 12 mm. pressure, has a sp. gr. 0·9764 at 18°/4°, and solidifies when cooled ; it is reduced by sodium and alcohol to *p*-ethylphenetole, the *sulphonic acid* of which crystallises from benzene in plates and melts at 82—84° and the *sulphonamide* crystallises from dilute alcohol in colourless, glistening needles and melts at 118°.

3 : 4-*Methylenedioxy*-1-*a*-*hydroxyethylbenzene*,

$$CH_2{:}O_2{:}C_6H_4\cdot CHMe\cdot OH,$$

is a clear, viscous oil, which boils at 137—138° under 14 mm. pressure, has a sp. gr. 1·2204 at 18°/4°, and n_D 1·5483 ; it does not solidify when cooled, and is oxidised by chromic acid to acetylpiperone ; the phenylurethane crystallises from alcohol in stout pyramids and melts at 65—67°. *Vinylcatechol methylene ether*, $CH_2{:}O_2{:}C_6H_4\cdot CH{:}CH_2$, is a mobile oil which boils at 107—108° under 15 mm. pressure, thickens when heated to 160° and becomes a hard glass when cooled ; it has a sp. gr. 1·1488 at 18°/4°, n_D 1·5802, and is reduced by sodium and alcohol to *ethylcatechol methylene ether*, $CH_2{:}O_2{:}C_6H_4Et$, a colourless oil which boils at 92—93° under 17 mm. and at 212—213° under 759 mm. pressure. T. M. L.

Formation of Nitroso-compounds of Polyhydroxylic Phenols. JACQUES POLLAK (*Chem. Centr.*, 1903, ii, 829 ; from *Verh. Vers. Deutsch. Naturf. Aerzte*, 1902, ii, 1, 80—84).—It is not necessary to assume that in the formation of *iso*nitroso-orcinol (Henrich, Abstr., 1901, i, 64) the group NOH enters between two OH groups, for *iso*nitroso-

orcinol may have a constitution, $OC<\genfrac{}{}{0pt}{}{CH{=}CMe}{CH{:}C(OH)}>C{:}N{\cdot}OH$, analogous to that of *iso*nitrosophloroglucinol methyl ether (Abstr., 1903, i, 252). *iso*Nitroso-orcinol monomethyl ether would then have the formula $OMe{\cdot}C<\genfrac{}{}{0pt}{}{CH{:}CMe}{CH{-}CO}>C{:}N{\cdot}OH$. The first N·OH group is thus placed, in accordance with Kostanecki's generalisation, in the ortho-position with regard to one OH group and in the para-position to the other; the second N·OH group would enter between two OH groups.

E. W. W.

Phenol Ethers. III. Constitution of Myristicin. HERMANN THOMS (*Ber.*, 1903, **36**, 3446—3451).—Myristicin contains an allyl group in place of the butenyl group originally postulated by Semmler (Abstr., 1892, 311), and has the constitution:

$$C_3H_5{\cdot}C_6H_2(OMe)<\genfrac{}{}{0pt}{}{O}{O}>CH_2\ [C_3H_5 : OMe : O_2CH_2 = 1 : 3 : 4 : 5].$$

When boiled with alcoholic potash, it is converted into iso*myristicin*, in which the allyl group is converted into a propenyl group; *iso*myristicin crystallises from dilute alcohol in small, colourless prisms and melts at 44—45°; Semmler's myristicin had been heated with sodium in the course of preparation, solidified when cooled, and gave a crystalline dibromide; it is therefore probable that it consisted largely of *iso*myristicin; the myristicin used in the present research could not be crystallised and did not give a crystalline dibromide. A small quantity of the phenol, $C_3H_5{\cdot}C_6H_2(OMe)(OH){\cdot}O{\cdot}CH_2{\cdot}OEt$, is produced with the *iso*myristicin.

iso*Myristicin dibromide*, $CHMeBr{\cdot}CHBr{\cdot}C_6H_2(OMe){:}O_2{:}CH_2$, prepared by the action of bromine on an ethereal solution of *iso*myristicin at −18°, crystallises from light petroleum in silky needles and melts at 109°.

Dibromomyristicin dibromide, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}C_6Br_2(OMe){:}O_2{:}CH_2$, separates from alcohol as a white, crystalline powder and melts at 130°. *Dibromo*iso*myristicin dibromide*, $C_3H_5Br_2{\cdot}C_6Br_2(OMe){:}O_2{:}CH_2$, crystallises from alcohol in colourless needles and melts at 156°.

Dihydromyristicin, $OMe{\cdot}C_6H_2Pr^{\alpha}{:}O_2{:}CH_2$, boils at 149—150° under 17 mm. pressure. 5-*Methoxy*-3-*propylphenol*, $OMe{\cdot}C_6H_3Pr^{\alpha}{\cdot}OH$, produced as a by-product in the reduction, boils at 160—161° under 17 mm. pressure, and has a sp. gr. 1·0598 at 20°. Its methyl ether, 3 : 5-*dimethoxypropylbenzene*, $C_6H_3Pr^{\alpha}(OMe)_2$, boils at 136—137° under 16 mm. pressure, has a sp. gr. 1·0194 at 19°, and is isomeric with dihydromethyleugenol.

*iso*Myristicin is oxidised by potassium permanganate to Semmler's myristicinaldehyde and myristic acid. T. M. L.

Phenol Ethers. IV. The Phenol Ether of the Essential Oil of French Parsley Seeds. HERMANN THOMS (*Ber.*, 1903, **36**, 3451—3456).—The German oil solidifies when cooled owing to separation of apiole, but the French oil, a mobile, pale-yellow, fragrant liquid of sp. gr. 1·017, and $[\alpha]_D$ −5·7° at 20°, remains liquid. Sodium carbonate extracts from the latter 0·0804 per cent. of palmitic acid,

whilst potassium hydroxide extracts 0·0516 per cent. of mixed phenols; sodium hydrogen sulphite separates only traces of aldehydes and ketones. The residue was fractionally distilled at first under atmospheric and then under reduced pressures. The first fraction consisted chiefly of pinene, but the third fraction yielded a tetrabromide, $OMe\cdot C_{10}H_7O_2Br_4$, identical with dibromomyristicin dibromide, and gave crystals of *iso*myristicin when heated with alcoholic potash; it therefore consists largely of myristicin; the small sixth fraction, when cooled, yielded crystals of apiole (methoxymyristicin).

Both the French and the German oils are obtained from *Petroselinum sativum* (parsley); the German fruit is slightly smaller than the French, but has exactly the same anatomical structure; the production of apiole in one case and myristicin in the other is perhaps due to differences in cultivation. T. M. L.

Preparation of Pentahydroxybenzene. FRANZ WENZEL and HUGO WEIDEL (*Chem. Centr.*, 1903, ii, 829—830; from *Verh. Vers. Deut. Naturf. Aerzte*, 1902, ii, 1, 88—89).—When the diethyl ether of styphnic acid, prepared by the action of nitro-sulphuric acid on resorcinol diethyl ether, is reduced by means of tin and hydrochloric acid, triaminoresorcinol diethyl ether is formed, and this substance, when boiled with water, yields the diethyl ether of pentahydroxybenzene. *Pentahydroxybenzene*, prepared by the action of hydriodic acid on the diethyl ether, crystallises from concentrated hydriodic acid in colourless crystals and is very readily soluble in water, but almost insoluble in organic solvents. E. W. W.

Abnormal Condensation of Trioxymethylene and certain Aromatic Organomagnesium Compounds. MARC TIFFENEAU and RAYMOND DELANGE (*Compt. rend.*, 1903, **137**, 573—575. Compare Abstr., 1903, i, 819).—The alcohol obtained by condensing trioxymethylene and magnesium benzyl chloride is not the normal product, benzylcarbinol, as stated by Grignard (Abstr., 1902, i, 198), but the isomeric *o*-tolylcarbinol. The two alcohols have similar boiling points, that of *o*-tolylcarbinol being 219° under the ordinary pressure and 119—120° under 14—15 mm.; but whereas *o*-tolylcarbinol is a crystalline solid melting at 35°, benzylcarbinol is a liquid which does not solidify at $-20°$. The phenylurethane derivative of *o*-tolylcarbinol melts at 79°, that of benzylcarbinol at 80°, whilst a mixture of the two melts at 70°.

This abnormal reaction between trioxymethylene and magnesium benzyl chloride is not due to the latter reacting as its isomeride, magnesium *o*-tolyl chloride $C_6H_4\cdot Me\cdot MgCl$, because on treatment with carbon dioxide it gives a yield of 60 per cent. of phenylacetic acid, according to the equation $C_6H_5\cdot CH_2\cdot MgCl + CO_2 + H_2O = C_6H_5\cdot CH_2\cdot CO_2H + MgCl\cdot OH$. The authors therefore suggest that this particular condensation is of the same type as that whereby the primary aromatic alcohols are obtained from formaldehyde and the arylhydroxylamines or sodium phenoxides, the following equation representing the reaction: $C_6H_5\cdot CH_2\cdot MgCl + HCHO = OH\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot MgCl \longrightarrow C_6H_4Me\cdot CH_2\cdot OMgCl$. The abnormal behaviour is peculiar to

trioxymethylene, the other aldehydes and ketones giving the normal product; thus magnesium benzyl chloride gives, with paracetaldehyde, benzylmethylcarbinol, $C_6H_5\cdot CH_2\cdot CHMe\cdot OH$, and with acetone, benzyldimethylcarbinol, $C_6H_5\cdot CH_2\cdot CMe_2\cdot OH$ (Grignard, Abstr., 1900, i, 382). M. A. W.

Cholesterol. ADOLF WINDAUS (*Ber.*, 1903, **36**, 3752).—The compound previously described as hydroxycholestanonol (*Habilitationsschrift, Freiburg*, 1903) and formulated as $C_{27}H_{44}O_3$ is now described as *cholestanonol* and formulated as $C_{27}H_{44}O_2,H_2O$; it is prepared by reducing with zinc dust and acetic acid a compound, $C_{27}H_{42}O_6N_2$, formed by oxidising cholesterol with fuming nitric acid, the whole of the nitrogen being eliminated in the form of ammonia; cholestanonol crystallises from 75 per cent. alcohol, melts at 142—143°, and contains a carbonyl and a secondary hydroxyl group. The *formyl* derivative, $C_{28}H_{44}O_3$, crystallises from alcohol in stout needles and melts at 104—105°. The *acetyl* derivative, $C_{29}H_{46}O_3$, crystallises from alcohol in long prisms and melts at 128°. The *benzoyl* derivative, $C_{34}H_{48}O_3$, crystallises from acetone, melts at 173°, and is very sparingly soluble in alcohol. The *nitrophenylhydrazone*, $C_{33}H_{49}O_3N_3,C_2H_5\cdot OH$, separates from alcohol in feathery crystals and melts at 194°.

Cholestanonol is oxidised by chromic acid to *cholestandione*, $C_{27}H_{42}O_2$, a diketone which crystallises from alcohol in needles, melts at 169°, and does not reduce ammoniacal silver nitrate. The *dioxime*, $C_{27}H_{44}O_2N_2$, crystallises from alcohol and melts and decomposes at 205°.

Further oxidation with chromic acid yields a dibasic ketonic *acid*, $C_{27}H_{42}O_5$, which crystallises from 70 per cent. acetic acid or from benzene, melts (not quite sharply) at 217—219°, and decomposes at this temperature with liberation of gas. The *magnesium* salt was obtained in minute, felted needles. The *methyl* ester, $C_{29}H_{46}O_5$, crystallises from methyl alcohol and melts at 113—114°, its *oxime* crystallises from methyl alcohol and melts at 76°. The *anhydride* was prepared, but melted irregularly between 170° and 187° and contained carbon and hydrogen in excess of the amounts required for the formula $C_{29}H_{40}O_4$.

T. M. L.

Cholesterol. VI. JULIUS MAUTHNER and WILHELM SUIDA (*Monatsh.*, 1902, **24**, 648—668. See Abstr., 1894, i, 326—486; 1896, i, 425; 1897, i, 31; 1903, i, 625).—In ethereal solution, with nitrogen trioxide, cholesterol forms a derivative, $C_{27}H_{43}O_2N$, which crystallises in white needles, melts at 94—95°, decomposes slowly at 120°, evolves brown vapours when heated, is stable towards potassium hydroxide, does not form an additive compound with bromine, gives Liebermann's nitroso-reaction and the cholesterol reaction, and yields cholesterol when boiled with alcohol. Cholesteryl acetate and chloride do not react with nitrogen trioxide in ethereal solution.

When treated with nitrous acid, cholesteryl acetate yields *nitrocholesteryl acetate*, $C_{29}H_{45}O_4N$, which crystallises in leaflets or flat needles, melts at 101—102°, and does not form an additive compound with bromine. On reduction with zinc and glacial acetic acid, nitrocholesteryl acetate yields *cholestanonyl acetate*, $C_{27}H_{43}O_2\cdot OAc$ (com-

pare Windaus, *Habilitationschrift*, *Freiburg*, 1903), which crystallises in flat prisms or leaflets, melts at 127°, evolves hydrogen bromide when acted on by bromine in carbon disulphide solution, and forms a p-*nitrophenylhydrazone*, $C_{35}H_{51}O_4N_3$, which crystallises in golden needles and melts at 144°.

Cholestanonol, $C_{27}H_{44}O_2$, obtained on hydrolysis of the acetate, crystallises in delicate, glistening needles, melts at 140°, and yields a p-*nitrophenylhydrazone*, $C_{33}H_{49}O_3N_3$, which crystallises in golden needles and melts at 195°.

Cholestanonol probably contains the grouping ·CO·CH⁚ in place of the grouping ·CH⁚C⁚ in cholesterol.

Chlorocholestanone, $C_{27}H_{43}OCl$, formed by reduction of nitrocholesteryl chloride, crystallises in delicate, colourless, glistening needles, and melts at 128·5—129°.

The product obtained on acting with chlorine on a mixture of cholesteryl chloride and half its weight of iodine in chloroform solution is apparently a mixture of two compounds, $C_{27}H_{35}Cl_{11}$ and $C_{27}H_{34}Cl_{12}$. Half of the chlorine is removed on treatment with alcoholic sodium hydroxide, and reduction of the resulting substance with zinc dust and glacial acetic acid leads to a substance containing 4 chlorine atoms.

The action of chlorine on the hydrocarbon, $C_{19}H_{28}$ (see Abstr., 1896, i, 426), in the presence of iodine leads to the formation of a mixture of chlorinated products. The part soluble in ether forms long, colourless needles and melts at 213—214°. Oily products, obtained on distillation of the chloro-compounds with lime, boil between 60° and 235° and give aldehyde reactions. The fractions boiling between 150° and 235° lose hydrogen chloride on distillation under the ordinary pressure.

When heated over a free flame, cholesteryl chloride yields cholesterylene, a hydrocarbon $C_{19}H_{28}$, and hydrocarbons C_8H_{16}(?) and C_8H_{18}(?). When the chloride is heated in a bath, there is also formed a hydrocarbon, $C_{20}H_{28}$(?), which boils at 241—265° under 42 mm., and a hydrocarbon, $C_{23}H_{34}$(?), which boils at 270—286° under 37—40 mm. pressure.

Cholesterol and oxalic acid in ethereal solution form *cholesterol oxalate*, $(C_{27}H_{44}O)_2,C_2H_2O_4$, which crystallises in flat needles, sinters at 172°, and melts at 200°.

Cholesteryl oxalate, $(C_{27}H_{43})_2C_2O_4$, formed by heating cholesterol and oxalic acid together at 195—200°, crystallises in colourless, matted needles, sinters at 215°, melts at 224°, and decomposes at 240°.

Cholesterylene is formed by the distillation of cholesteryl chloride with lime or by heating cholesteryl chloride with quinoline.

G. Y.

Preparation of Anthranilic Acid and *N*-Alkylated Anthranilic Acids. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 145604).—The replacement of the chlorine atom of *o*-chlorobenzoic acid in presence of metallic copper or copper salts (compare Abstr., 1903, i, 754) also takes place readily with ammonia or alkylamines. Ammonia at 125° under pressure forms anthranilic acid, together with the sparingly soluble *diphenylamine*-2 : 2′-*dicarboxylic acid*. *Ethyl-*

anthranilic acid, $NHEt{\cdot}C_6H_4{\cdot}CO_2H$, from ethylamine, crystallises from dilute alcohol in colourless prisms melting at 152—153°.

C. H. D.

Sulphonic Acids of Phenyl- and Naphthyl-anthranilic Acids. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 146102. Compare preceding abstract).—*o*-Chlorobenzoic acid reacts readily with sulphonic acids of the benzene or naphthalene series on heating the alkali salts in presence of copper or copper salts. Thus, sulphanilic acid forms 4′-sulphodiphenylamine-2-carboxylic acid, the *sodium hydrogen* salt of which forms white leaflets decomposing at 265—266° when heated rapidly. The *barium* salt of 3′-sulphodiphenylamine-2-carboxylic acid, from metanilic acid, contains water of crystallisation, which is only slowly lost on heating. The *sodium hydrogen* salt of 3′-sulpho-*p*-tolylamino-2-benzoic acid, from *p*-toluidine-2-sulphonic acid, is sparingly soluble in water and is not completely fused at 280°; the corresponding salt of 4′-sulpho-*o*-tolylamino-2-benzoic acid, from *o*-toluidine-5-sulphonic acid, melts and decomposes at 265—266°.

Similar salts, prepared from a number of aminosulphonic acids of the benzene and naphthalene series, are described. C. H. D.

***o*-Sulphaminebenzoic and *o*-Carbaminebenzenesulphonic Acids.** Francis Daniel Wilson (*Amer. Chem. J.*, 1903, 30, 353—373).—By the action of sodium hydroxide on benzoicsulphinide, a nearly quantitative yield of *o*-sulphaminebenzoic acid, $CO_2H{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, is obtained. This acid crystallises in plates or needles and is soluble in alcohol or water; when heated slowly, it melts at 152°, but if heated rapidly melts at 159°. If heated in a tube in a current of dry air, it decomposes at 128° with formation of benzoicsulphinide. The salts of *o*-sulphaminebenzoic acid form well-defined crystals, and, with the exception of the mono-silver, potassium, and ammonium salts, all contain water of crystallisation; when heated, they decompose with formation of benzoicsulphinide at a few degrees above the temperature at which they give off their water of crystallisation. The *sodium, potassium, calcium, barium, strontium, zinc, magnesium, copper, ammonium*, and *mono-* and *di-silver* salts are described. When the acid is heated with phosphorus oxychloride, it is completely converted into benzoicsulphinide. The *amide*, $NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, melts at 263°.

o-Carbaminebenzenesulphonic acid [*o*-sulphobenzamide],

$$NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_3H,$$

obtained by treating the potassium hydrogen salt of *o*-sulphobenzoic acid with ammonium thiocyanate, crystallises from water in large, transparent crystals, is soluble in alcohol, melts at 193—194° (uncorr.), and decomposes when heated at 125°. The potassium, mono- and *tri-silver*, sodium, *barium, strontium, calcium, zinc, magnesium, copper*, and ammonium salts were prepared and analysed. The *chloride*, $NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}SO_2Cl$, obtained by heating the potassium salt with phosphorus oxychloride at 100° for half an hour, crystallises in thick, opaque plates, and melts at 63°. If the mixture of the potassium salt and phosphorus oxychloride is merely warmed, potassium

o-cyanobenzenesulphonate is produced. When the chloride is treated with a solution of ammonium hydroxide, a white *substance* is formed, which crystallises in opaque plates and does not melt when heated to the boiling point of sulphuric acid. E. G.

Action of Phenols and Alcohols on the Chlorides of *p*-Nitro-*o*-sulphobenzoic Acid. VICTOR JOHN CHAMBERS (*Amer. Chem. J.*, 1903, 30, 373—392).—The observation of Henderson (Abstr., 1901, i, 208), that by the action of phenol on the symmetrical chloride of *p*-nitro-*o*-sulphobenzoic acid the diphenyl ester is produced, is now confirmed. When the unsymmetrical chloride is heated with phenol, the sulphonic chloride of phenyl *p*-nitrobenzoate is formed, but no diphenyl ester is obtained.

The *sulphonic chloride* of phenyl-*p*-nitrobenzoate,

$$CO_2Ph\cdot C_6H_3(NO_2)\cdot SO_2Cl,$$

crystallises in light brown needles and melts at 145—147°. When this substance is treated with dilute hydrochloric acid, *p*-nitro-*o*-sulphobenzoic acid is produced, whilst if it is boiled with water both the free acid and the monophenyl ester are obtained. By the action of barium hydroxide, the chloride is converted into barium *p*-nitro-*o*-sulphobenzoate and the diphenyl ester. When treated with ammonia, it yields *p*-nitrobenzoicsulphinide and the diphenyl ester, whilst with aniline the anil is produced. By the action of alcohols, the chloride is converted into the monophenyl ester. *Barium phenyl* p-*nitro*-o-*sulphobenzoate* and the corresponding *potassium* salt are described.

When alcoholic potassium hydroxide is added slowly to an alcoholic solution of the symmetrical chloride and *o*-cresol, a *substance* is obtained which crystallises in needles, melts at 90°, and is probably di-*o*-tolyl *p*-nitro-*o*-sulphobenzoate. By the action of *o*-cresol on the unsymmetrical chloride, the o-*sulphonic chloride* of *o*-tolyl *p*-nitrobenzoate, $CO_2(C_7H_7)\cdot C_6H_3(NO_2)\cdot SO_2Cl$, is produced, which crystallises in white plates and melts at 150°.

If a mixture of the symmetrical chloride and *p*-cresol is treated with dilute potassium hydroxide, *di*-p-*tolyl* p-*nitro*-o-*sulphobenzoate* is produced, which melts at 118°. By the action of *p*-cresol on the unsymmetrical chloride, the o-*sulphonic chloride* of *p*-tolyl *p*-nitrobenzoate is obtained, which crystallises in small needles or prisms and melts at 152° (uncorr.).

o-Nitrophenol reacts with each chloride to form *di*-o-*nitrophenyl* p-*nitro*-o-*sulphobenzoate*, which crystallises in slender needles and melts at 164°.

p-Nitrophenol reacts with both chlorides in a similar manner with the production of the *di*-p-*nitrophenyl* ester, which crystallises in thick needles and melts at 152°.

Resorcinol and quinol react with both chlorides, but no definite product was isolated.

Di-β-naphthyl p-*nitro*-o-*sulphobenzoate*, obtained by the action of *β*-naphthol on the unsymmetrical chloride, crystallises in white needles and melts at 134°.

p-Aminophenol reacts with the unsymmetrical chloride, but no definite product could be isolated.

By the action of phenol on the symmetrical chloride in the presence of ammonia, diphenyl *p*-nitro-*o*-sulphobenzoate is produced together with *phenyl* p-*nitro*-o-*sulphaminebenzoate*, $CO_2Ph\cdot C_6H_3(NO_2)\cdot SO_2\cdot NH_2$, which crystallises in prisms and melts at 135°, and by the action of dilute alkali or water is converted into *p*-nitrobenzoicsulphinide. When the unsymmetrical chloride is treated in the same way, phenyl *p*-nitro-*o*-sulphaminebenzoate is not obtained.

It has been shown by Henderson (*loc. cit.*) that the symmetrical chloride reacts with alcohols with the formation of alkyl esters. When the unsymmetrical chloride is treated with methyl alcohol, the sulphonic chloride of methyl *p*-nitrobenzoate, $CO_2Me\cdot C_6H_3(NO_2)\cdot SO_2Cl$, is produced, which crystallises in small, thick prisms, melts at 82°, and when boiled with alcohol is converted into methyl *p*-nitro-*o*-sulphobenzoate. *Sodium methyl* p-*nitro*-o-*sulphobenzoate*,

$$CO_2Me\cdot C_6H_3(NO_2)\cdot SO_3Na,$$

crystallises in transparent plates; the corresponding *potassium* salt was prepared.

The *sulphonic chloride* of ethyl *p*-nitrobenzoate crystallises in white needles, melts at 68°, and when boiled with alcohol is converted into ethyl *p*-nitro-*o*-sulphobenzoate. *Barium ethyl* p-*nitro*-o-*sulphobenzoate* and the corresponding potassium salt were prepared and analysed.

The *sulphonic chloride* of propyl *p*-nitrobenzoate forms large, thin plates, melts at 76°, and is converted by boiling alcohol into propyl *p*-nitro-*o*-sulphobenzoate. *Barium propyl* p-*nitro*-o-*sulphobenzoate* and the corresponding potassium salt were prepared and analysed. E. G.

trans-Phenyltrimethylenecarboxylic Acid. EDUARD BUCHNER and JOSEF GERONIMUS (*Ber.*, 1903, 36, 3782—3786).—*Ethyl* trans-*2-phenyltrimethylenecarboxylate*, $C_6H_5\cdot C_3H_4\cdot CO_2Et$, prepared by heating styrene with ethyl diazoacetate at 100° during 12—15 hours, boils at 144—148° under 15 mm. pressure, crystallises from light petroleum in long, colourless needles, and melts at 39°. The *acid* separates from hot water in silky needles, melts at 105°, and is not altered by permanganate. The *amide* crystallises from hot water in colourless, glistening flakes and melts at 187—188°. The *calcium* salt, $(C_{10}H_9O_2)_2Ca,2H_2O$, was crystallised from water, dried, and distilled; no phenyltrimethylene was produced, but styrene and allylbenzene were detected in the distillate. *Nitrophenyltrimethylenecarboxylic acid*, $NO_2\cdot C_6H_4\cdot C_3H_4\cdot CO_2H$, crystallises from water and melts at 154°. The *amino*-compound was not analysed; its hydrochloride separates from alcohol in yellow needles and melts (not sharply) at 173—185°; the amino-acid is oxidised by permanganate to *trans*-1 : 2-trimethylenedicarboxylic acid. T. M. L.

Diaminomethyldiphenylcarboxylic Acid. CHEMISCHE FABRIK VORM. WEILER-TER-MEER (D.R.-P. 145063).—When *o*-nitrotoluene is reduced by heating with iron or zinc and sodium hydroxide solution at 100°, *o*-azoxytoluene is precipitated on dilution, and on addition of acids *toluene*-o-*azobenzoic acid* separates, crystallising from toluene in orange-red needles with blue lustre, and melting at about 148°. On warming with sodium hydroxide and zinc dust until decolorised, further reduction to *toluene*-o-*hydrazobenzoic acid*, melting at about 136°,

takes place. On warming with strong hydrochloric acid and adding sodium hydroxide, *diaminomethyldiphenylcarboxylic acid*,

$$NH_2\cdot C_6H_4Me\cdot C_6H_4(NH_2)\cdot CO_2H,$$

is precipitated as an oil, rapidly solidifying, and crystallising from water or dilute alcohol in slender, white needles which melt and evolve carbon dioxide at 183°. It forms easily soluble salts with acids and sparingly soluble salts with bases. The *sodium* salt forms small needles, of which 8·7 parts dissolve in 100 parts of water at 20°. The *barium* salt crystallises in leaflets, of which 2·5 parts dissolve in 100 parts of water at 20°. C. H. D.

Pseudonitrosites. HEINRICH WIELAND (*Annalen*, 1903, **329**, 225—268. Compare Abstr., 1903, i, 764).—To the pseudonitrosites which are obtained from phenyl-substituted olefines (*loc. cit.*), Angeli (Abstr., 1893, i, 355; 1896, i, 295) gave the configuration

$$\begin{array}{ccc} \cdot CH & — & CH\cdot \\ | & & | \\ N & -O- & N \\ | & & | \\ O & —— & O \end{array},$$

but on account of the various reactions detailed later, it is thought that these substances are best represented as dimolecular compounds of the form $NO_2\cdot CH\colon CH\cdot(N_2O_2)\cdot CH\colon CH\cdot NO_2$. When boiled with alcohol, the pseudonitrosites are converted into "nitro-oximes," thus the derivative of methyl phenyl*iso*crotonate yields the oxime of methyl benzoylnitropropionate, $OH\cdot N\colon CPh\cdot CH(NO_2)\cdot CH_2\cdot CO_2Me$; the nitro-oximes are relatively stable, and are hydrolysed to hydroxylamine and nitro-ketones (compare Abstr., 1903, i, 836, 837).

Acetic anhydride brings about the same decomposition, but in the presence of a few drops of sulphuric acid the oxime group is eliminated and replaced by an acetyl group, thus:

$$OAc\cdot CHPh\cdot CH(NO_2)\cdot CH_2\cdot CO_2Me.$$

Sulphuric acid alone produces the unsaturated nitro-ester,

$$CHPh\colon C(NO_2)\cdot CH_2\cdot CO_2Me.$$

By alkali hydroxides in the presence of alcohols, the pseudonitrosites are decomposed into hyponitrite and the alkali salt of the ether, $\cdot CH(OMe)\cdot CMe\colon NO_2K$, which, on acidifying, is decomposed into methyl alcohol and a β-nitropropylene derivative, $\cdot CH\colon C(NO_2)\cdot CH_3$; when the pseudonitrosites are heated with alkali hydroxides, nitroethane and an aromatic aldehyde are formed.

Aromatic bases give anilino-nitro-derivatives, thus from the nitrosite of methyl phenyl*iso*crotonate, methyl β-nitro-γ-anilino-γ-phenylbutyrate, $NHPh\cdot CHPh\cdot CH(NO_2)\cdot CH_2\cdot CO_2Me$, is formed.

The pseudonitrosites are converted, under certain conditions, into glyoxime peroxides, $\begin{array}{ccc} \cdot C & —— & C\cdot \\ \| & & \| \\ N & \cdot O\cdot O\cdot & N \end{array}$; these substances are, however, most readily formed when the nitro-oximes, the decomposition products of the pseudonitrosites, are set free from their salts. It is supposed that the salts of the nitro-oximes are nitronates, and that the free nitronic acid, $\begin{array}{ccc} \cdot C & ——— & CMe \\ \| & & \| \\ N\cdot OH & & HO_2N \end{array}$, loses water, changing into the peroxide.

A comparison of the behaviour of the nitrosites and the pseudo-

nitrosites has led to the view that these two classes of substances differ in that the nitrosites are nitrites, whilst the pseudo-compounds are nitro-derivatives, thus, amylene nitrosite is represented by the formula $N_2O_2(CHMe{\cdot}CMe_2{\cdot}ONO)_2$, and anetholpseudonitrosite by the formula $[OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CH_2{\cdot}NO_2)]_2N_2O_2$. Thus the nitrosites, with aniline, yield the anilino-oximes, $\cdot C(:NOH){\cdot}CH(NHPh)\cdot$, whilst the pseudonitrosites give anilino-nitro-compounds,

$$\cdot CH(NHPh){\cdot}CH(NO_2)\cdot\ ;$$

with potassium methoxide, the nitrosites give compounds of the type $\cdot C(:NOK){\cdot}CH(OMe)\cdot$, and the pseudonitrosites $\cdot CH(OMe){\cdot}C(:NO_2K)\cdot$.

The constitution of the bisnitroso-group is discussed (compare Piloty, Abstr., 1902, i, 734), and Thiele's theory of "partial" valency is introduced in order to explain the unstable dimolecular nitroso-compounds.

The *pseudonitrosite* of methyl phenyl*iso*crotonate,

$$N_2O_2[\cdot CHPh{\cdot}CH(NO_2){\cdot}CH_2{\cdot}CO_2Me]_2,$$

is prepared by leading nitrous fumes (from white arsenic and nitric acid) into an ethereal solution of the ester, when a white, crystalline powder is precipitated; it is purified by washing with ether, and then melts and decomposes at 118°; it is changed by all solvents except chloroform. Phenol and sulphuric acid give a dark blue coloration, which becomes bordeaux-red on dilution; it dissolves in alcoholic alkali with evolution of nitrous oxide and formation of a yellow solution; concentrated sulphuric acid causes the evolution of nitrous oxide. The *nitro-oxime* of methyl phenyl*iso*crotonate,

$$OH{\cdot}N{:}CPh{\cdot}CH(NO_2){\cdot}CH_2{\cdot}CO_2Me,$$

is prepared from the nitrosite by boiling with alcohol; on adding water, a solid separates which crystallises from benzene in needles melting and decomposing at 128°, and is soluble in alkali hydroxides but not in carbonates; when boiled with acids, hydroxylamine is set free. *Methyl β-nitro-γ-acetoxy-γ-phenylbutyrate*,

$$OAc{\cdot}CHPh{\cdot}CH(NO_2){\cdot}CH_2{\cdot}CO_2Me,$$

is obtained when the pseudonitrosite is treated with acetic anhydride containing a few drops of sulphuric acid, and forms large, prismatic crystals melting at 89°. *Methyl β-nitro-γ-anilino-γ-phenylbutyrate*, $NHPh{\cdot}CHPh{\cdot}CH(NO_2){\cdot}CH_2{\cdot}CO_2Me$, is prepared by heating the pseudonitrosite in alcoholic solution with aniline, forms colourless crystals melting at 122°, and yields a well-crystallised nitrosoamine. With phenylhydrazine, a reaction took place, but of the products, the phenylhydrazone of benzaldehyde was alone isolated.

Ammonium quadroxalate, $C_2O_4H(NH_4),C_2O_4H_2,2H_2O$, separates in large plates from the mother liquors obtained in the preparation of the pseudonitrosite; it melts and decomposes at 128°.

The *pseudonitrosite* of benzylideneacetone,

$$N_2O_2[\cdot CHPh{\cdot}CH(NO_2){\cdot}COMe]_2,$$

is obtained in colourless needles by leading nitrous fumes over an ethereal solution of benzylideneacetone; it becomes red at 100° and melts and decomposes at 109—110°. With phenol and sulphuric acid, it gives a cherry-red coloration which becomes blue when alkali is added. The *nitro-oxime* of benzylideneacetone (the *oxime* of benzoylnitroacetone), $OH{\cdot}N{:}CPh{\cdot}CHAc{\cdot}NO_2$, prepared by saturating a

solution of benzylideneacetone in benzene with nitrous fumes, crystallises in slender needles softening at 70°, and melting to a milky liquid at 84°, which becomes clear at 100°. By alcoholic potassium hydroxide it is decomposed into nitroacetophenoxime and acetic acid. When boiled with concentrated aqueous hydrogen chloride, it is converted into *phenylmethylnitroisooxazole*, $\begin{matrix} C(NO_2){:}CMe \\ | \quad\quad | \\ CPh{:}N{-}O \end{matrix}$, which crystallises in colourless, four-sided pyramids melting at 48°.

The pseudonitrosite of anethole,

$$(N_2O_2)[CH(C_6H_4{\cdot}OMe){\cdot}CHMe{\cdot}NO_2]_2,$$

prepared by adding sodium nitrite to an acetic acid solution of anethole (compare Tönnies, Abstr., 1881, 167), decomposes at about 120°, and by boiling with alcohol is converted into the corresponding *nitroxime*, which crystallises in needles melting at 87°. The latter is very readily converted into the glyoxime peroxide (m. p. 97°) in the manner described above (compare Tönnies, *loc. cit.*). *β-Nitroanethole*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CMe{\cdot}NO_2$, is prepared by adding the pseudonitrosite to an alcoholic solution of ammonia and crystallises in yellow needles melting at 48°. It is soluble in cold alkali hydroxides, but by hot solutions is converted into anisaldehyde. The nitroanethole is also formed by the carefully regulated action of alkali hydroxides on the pseudonitrosite, hyponitrous acid being at the same time produced.

When the anethole is treated in acetic acid solution with sodium nitrite, the temperature being allowed to rise, the glyoxime peroxide is formed together with the *amphi-dioxime* of anisylmethyl-1 : 2-diketone, $OMe{\cdot}C_6H_4{\cdot}C(NOH){\cdot}C(NOH){\cdot}CH_3$, which was isolated as a yellow solid melting and decomposing at 206°. K. J. P. O.

Benzonorcaradienecarboxylic Acid. EDUARD BUCHNER and STEPHAN HEDIGER (*Ber.*, 1903, 36, 3502—3509).—The reaction between ethyl diazoacetate and naphthalene is similar to that between ethyl diazoacetate and benzene (Braren and Buchner, Abstr., 1901, i, 85, 385). The naphthalene is heated at 140—145° on an oil-bath, and the ester is added very gradually; nitrogen is steadily evolved, and the product is isolated by fractional distillation under reduced pressure. *Ethyl benzonorcaradienecarboxylate*, $C_{10}H_8{:}CH{\cdot}CO_2Et$, is a viscid, colourless oil, becoming yellow in the air, boiling at 163—164° under 11 mm. pressure, and reducing an alkaline solution of potassium permanganate. It combines with bromine in chloroform solution, forming a *dibromide*, which crystallises from alcohol in colourless needles and melts at 95—96°. *Benzonorcaradienecarboxylic acid*, $\begin{matrix} CH{:}CH{\cdot}C\text{———————}CH \\ | \quad\quad\quad || \quad\quad\quad\quad\quad\quad | \\ CH{:}CH{\cdot}C{\cdot}CH{:}CH{\cdot}CH \end{matrix}{>}CH{\cdot}CO_2H$, prepared by hydrolysing the ester with sodium ethoxide and decomposing the sodium salt by acid, forms colourless crystals melting at 165—166°, insoluble in water, but dissolving readily in alcohol or benzene. The *amide* forms colourless crystals melting at 217°. The *dibromide* melts and decomposes at about 168°, and reacts with boiling water to form *bromohydroxybenzonorcarenecarboxylic acid*,

$$C_{11}H_9Br(OH){\cdot}CO_2H,$$

crystallising from ether in colourless needles melting and decomposing at 170—173°, and *dihydroxybenzonorcarenecarboxylic acid*,

$$OH\cdot CH<\begin{matrix}C_6H_4\text{——}CH\\ CH(OH)\cdot CH\end{matrix}>CH\cdot CO_2H,$$

melting at 203°, and forming a faintly yellow *diacetyl* derivative melting at 216°. Potassium permanganate oxidises an alkaline solution of benzonorcaradienecarboxylic acid, one benzene ring of the naphthalene nucleus being broken down, forming *carboxyphenyl trimethylene*-trans-1 : 2-*dicarboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CH<\begin{matrix}CH\cdot CO_2H\\ CH\cdot CO_2H\end{matrix},$$

which crystallises in yellowish-white needles melting at about 273—275°. Fuming nitric acid converts this into a *nitro-acid*, separating from dilute alcohol in greenish-yellow crystals decomposing at about 290°. Ferrous hydroxide and ammonia reduce this to the corresponding *amino-acid*, crystallising from water in faintly yellow needles decomposing at 259°, and being oxidised by potassium permanganate to trimethylene-*trans*-1 : 2 : 3-tricarboxylic acid, identical with that prepared by Buchner and Witter (Abstr., 1895, i, 269).

C. H. D.

Ethyl Diazoacetate and Toluene. Eduard Buchner and Leon Feldmann (*Ber.*, 1903, 36, 3509—3517).—Ethyl diazoacetate and toluene react together at 118°, forming *ethyl 4-methylnorcaradiene-carboxylate*, $\begin{matrix}CH{=}CH\cdot C\\ CMe\cdot CH\cdot C\end{matrix}>CH\cdot CO_2Et$, which boils at 122—126° under 15 mm. pressure, and reacts with cold aqueous ammonia, on long contact, with the formation of 4-*methylnorcaradienecarboxylamide*, crystalling from ether or hot water and melting at 131°. A portion of the original oil remains unattacked, and when hydrolysed by boiling with 30 per cent. sulphuric acid yields 4-*methyl*cyclo*heptatrienecarboxylic acid*, $C_7H_6Me\cdot CO_2H$, crystallising from boiling water in flat needles melting at 107—108°. The *amide* forms long needles melting at 99° Hydrolysis of the 4-methylnorcaradienecarboxylamide yields an amorphous compound, together with a small quantity of *p*-tolylacetic acid.

C. H. D.

Preparation of Bromoindigotin. Farbwerke vorm. Meister, Lucius, and Brüning (D.R.-P. 144249).—Indigo-white reacts with bromine at the ordinary temperature with development of heat and formation of hydrogen bromide. A bromoindigo-white is first produced, and may be isolated by employing only a small quantity of bromine and extracting with acetone, in which bromoindigo-white is soluble, whereas bromoindigotin remains undissolved. In the presence of an excess of bromine, the intermediate compound is oxidised to bromoindigotin, containing from 1 to 2 atoms of bromine in the molecule.

Bromoindigotin is a violet-blue powder and dissolves in concentrated sulphuric acid to a yellowish-green solution, slowly becoming

blue. In its behaviour towards organic solvents it resembles indigotin, but the solution in hot nitrobenzene, unlike that of indigotin, is not fluorescent. The shade produced in dyeing is more violet than that of indigotin. C. H. D.

Triphenylmethane Derivatives and their Oxidation Products, obtained from Tetramethyldiaminobenzhydrol and *m*-Ethoxybenzoic Acid, and its Amide, Methylamide, and Dimethylamide. Paul Fritsch (*Annalen*, 1903, 329, 66—81. Compare Abstr., 1897, i, 72).—m-*Ethoxybenzamide*, $OEt \cdot C_6H_4 \cdot CO \cdot NH_2$, prepared by heating together an intimate mixture of *m*-ethoxybenzoic chloride and ammonium carbonate, crystallises in needles melting at 139—139·5°. The corresponding *methylamide* is prepared by shaking a benzene solution of the acid chloride with a 33 per cent. solution of methylamine; it crystallises in needles melting at 64°. The *dimethylamide* is prepared in a similar manner and was only obtained as an oil.

The triphenylmethane derivatives were prepared by dissolving an intimate mixture of the acid or one of the foregoing amides and benzhydrol in 90 per cent. sulphuric acid, pouring the mixture on to ice after the benzhydrol had disappeared and neutralising the acid, when a mixture of isomeric bases was precipitated; from this, however, only one base could be isolated in small quantity; in this base, the condensation had taken place in the para-position to the ethoxy-group. *Tetramethyldiamino*-m-*ethoxytriphenylmethane*-o-*carboxylic acid*, $CH(C_6H_3 \cdot NMe_2)_2 \cdot C_6H_3(OEt) \cdot CO_2H$, is extracted from the mixture of bases by means of carbon disulphide, and crystallises from benzene in needles melting at 197—198°, and when quite free from the isomeric bases gives no coloration with chloranil. The corresponding *amide*, prepared by using *m*-ethoxybenzamide, crystallises in concentric groups of needles melting at 191—192°. The *methylamide*, prepared in a similar manner, crystallises in flattened prisms or needles melting at 185—186°. The *dimethylamide* forms quadratic crystals melting at 139—140°.

These triphenylmethane derivatives were oxidised by adding lead dioxide (1 mol.) to a very dilute ice-cold solution of the base (1 mol.) in hydrochloric acid (4 mols.); after half an hour, the lead was precipitated by sodium sulphate. From the carboxylic acid above mentioned, the *phthalein*, $CO{<}\underset{O}{\overset{C_6H_3(OEt)}{\longrightarrow}}{>}C(C_6H_4 \cdot NMe_2)_2$, was obtained by neutralising the acid mother liquor from which the lead had been precipitated, and crystallised from a mixture of carbon disulphide and petroleum in pale yellow, six-sided plates melting at 167—168°; it dissolves in acetic acid with a pale green coloration, rapidly becoming more intense on heating. When boiled with zinc dust and acetic acid, it is reconverted into the leuco-compound. From the carboxylamide, the *compound*,

$$CO{<}\underset{NH}{\overset{C_6H_3(OEt)}{\longrightarrow}}{>}C(C_6H_4 \cdot NMe_2)_2,$$

is obtained and crystallises in lustrous leaflets, rhombic plates, or long needles melting at 242—244°, which dissolves in acids with a deep

green coloration, and is not reduced by zinc dust and acetic acid. The corresponding *methylimide* is prepared in a similar manner and crystallises in prismatic leaflets melting at 181°; it cannot be reduced by zinc and acetic acid. From the corresponding dimethylamide, the *compound*, $OEt \cdot C_6H_3(CO \cdot NMe_2) \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot OH$, is obtained, and crystallises in rhombohedra melting at 188°; this dye colours wool a brilliant green.

In order to determine the constitution of these substances, the foregoing carboxylic acid was distilled with many times its weight of baryta in a stream of hydrogen, when the *base*, $OEt \cdot C_6H_4 \cdot CH(C_6H_4 \cdot NMe_2)_2$, was obtained and crystallised in colourless needles melting at 125°. The same base was also prepared by condensing *p*-ethoxybenzaldehyde with dimethylaniline in the presence of zinc chloride. K. J. P. O.

β-4-Dimethylamino-2-hydroxybenzoylpropionic Acid and its Application in Preparing Succinein Dyes. ARTHUR WEINSCHENK (*Zeit. Farb. Text. Chem.*, 1903, 2, 409—413).—*β-4-Dimethylamino-2-hydroxybenzoylpropionamide*,

$$NMe_2 \cdot C_6H_3(OH) \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2,$$

prepared by heating succinimide with *m*-dimethylaminophenol and boric acid at 150—175°, crystallises from pyridine in needles and melts and partially decomposes at 217—220°. On hydrolysis with alkali, it readily gives *β-4-dimethylamino-2-hydroxybenzoylpropionic acid*, which is a crystalline powder melting at 190°; when heated with resorcinol and concentrated sulphuric acid for $2\frac{1}{2}$ hours at 150—160°, it gives a *succinoresorcinorhodol*, whilst from pyrogallol under similar conditions a *succinopyrogallorhodol* is obtained. Both of these dyes yield crystalline salts; the colours they give are not fast to soap. W. A. D.

Esterification of *ortho*-Aldehydo-acids. RUDOLF WEGSCHEIDER, LEO KUŠY VON DÚBRAV and PETER VON RUŠNOV (*Monatsh.*, 1903, 24, 790—804. Compare Abstr., 1902, i, 619; 1903, i, 562).—Nitro-opianic acid is found to melt at 168·5—169·5°. Of the two methyl esters, that which is obtained by the action of methyl iodide on the silver salt and melts at 76—78° is the true ester. Fink's ester (*Ber.*, 1898, 31, 924), which is obtained on heating the acid with methyl alcohol, crystallises in white needles, melts at 181·5—182·5°, and is the ψ-methyl ester. Both methyl esters are only slightly hydrolysed by boiling water; when boiled with alcoholic potassium hydroxide, the ψ-methyl ester yields a *product* which forms yellow crystals, melts and decomposes at 260°, and is also obtained on boiling nitro-opianic acid with alcoholic potassium hydroxide.

Oxidation of the methyl ester with potassium permanganate in aqueous methyl alcoholic solution leads to the formation of nitrohemipinic acid and not of methyl hydrogen nitrohemipinate. Potassium permanganate has no action on the ψ-methyl ester in acetone or aqueous methyl alcoholic solution; a portion of the ψ-ester is hydrolysed by the water.

The formation of a second ethyl ester of nitro-opianic acid has not yet been accomplished (compare Prinz, Abstr., 1882, 402). G. Y.

Derivatives of Taurine and Synthesis of Taurocholic Acid. SIEGFRIED TAUBER (*Beitr. chem. Physiol. Path.*, 1903, **4**, 323—330).—Finely divided taurine reacts with benzoic anhydride at 250° yielding a *compound*, $C_{15}H_{20}ON_2S_2$, probably according to the equation $C_{14}H_{10}O_3 + 2C_2H_7O_3NS = C_{15}H_{20}ON_2S_2 + 3CO_2 + 2H_2O$. The compound is precipitated from its alcoholic solution by the addition of acetone, melts at 175°, and is readily soluble in alcohol, ether, or hot light petroleum. Taurine and phthalic anhydride yield a *compound*, $C_{25}H_{29}O_{16}N_3S_2,7H_2O$, which crystallises from acetone in long, thin, hexagonal plates, melts at 50°, and is readily soluble in water.

Unlike the majority of amino-fatty acids, taurine cannot be converted into its esters by Curtius's method. Phenylcarbimide does not combine with taurine, and it has been found impossible to introduce acyl groups into the taurine molecule.

Taurine and sodium cholate react at 265° yielding a product which appears to be identical with sodium taurocholate. J. J. S.

Synthesis of a Dicyclic Ring-compound. GUSTAV KOMPPA and TAVI HIRN (*Ber.*, 1903, **36**, 3610—3612).—Homo*iso*phthalic acid, prepared by hydrolysing *m*-cyanobenzyl cyanide (Reinglass, Abstr., 1891, i, 1344) with sulphuric acid, crystallises from water in flat, radiating groups of needles or broad tablets, melting at 184—185°, and is readily soluble in alcohol, sparingly in ether, almost insoluble in benzene or chloroform (compare Allen and Underwood, Abstr., 1884, 587). Sodium amalgam reduces it to a tetrahydro-acid, which, by the addition of hydrogen bromide and further reduction with sodium amalgam, is converted into *hexahydrohomo*iso*phthalic acid*,

$$CO_2H\cdot CH{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}CH\cdot CH_2\cdot CO_2H,$$

which crystallises from water in small, thick needles melting at 158°, but sintering at a much lower temperature when slowly heated, dissolving readily in acetone, sparingly in water, benzene, or light petroleum. When mixed with lime and distilled, it forms *keto*dicyclo-1 : 2 : 3-*octane*,

$$\begin{array}{l} CH_2{-}CH{-}CH_2 \\ \;|\qquad\;\; | \qquad\; | \\ CH_2 \quad CH_2 \quad | \\ \;|\qquad\;\; | \qquad\; | \\ CH_2{-}CH{-}CO \end{array}$$

, which forms a tough, white mass smelling like camphor and melting at 157—158°. The *semicarbazone* crystallises in microscopic needles melting at 189—190°, and dissolves readily in methyl or ethyl alcohol, sparingly in water, ether, or benzene. C. H. D.

Constitution of Derivatives of Santonin. EDGAR WEDEKIND (*Ber.*, 1903, **36**, 3461—3464).—Controversial, in reply to Francesconi (Abstr., 1903, i, 830). T. M. L.

Action of Light and of Alkalis on Santonin and its Derivatives. Photosantoninic Acid. LUIGI FRANCESCONI and G. MAGGI (*Gazzetta*, 1903, **33**, ii, 65—80).—On exposing a solution of santonin

(1 mol.) in normal potassium hydroxide solution (3 mols.) to sunlight for two months, it was found to yield a compound, $C_{30}H_{42}O_9$, identical with that described by Sestini (Abstr., 1877, i, 471), to which the authors give the name photosantoninic acid; it separates from acetic acid in crystals, softens at 200°, begins to colour at 230°, melts at 258—260°, and it has $[\alpha]_D$ $-9{\cdot}88°$. Its *barium* and *silver* salts were prepared, and also its *diethyl* ester, which separates from light petroleum or aqueous alcohol in white crystals melting at 132°. The action of acetic anhydride on the acid yields the *acetyl* derivative of the dilactone of photosantoninic acid, $C_{32}H_{40}O_8$, which forms white, acicular crystals melting at 199—201°.

From the results of these and previous researches, the authors draw the following conclusions: (1) the action of hydrochloric acid on santonin yields desmotroposantonin, whilst under the influence of light a resinous substance, soluble in sodium carbonate, is also formed. (2) Santonic acid is not acted on by hydrochloric acid and light. (3) Potassium hydroxide and light have no action on santonic or photosantonic acid, whilst with *iso*photosantonic acid alone, or mixed with photosantonic acid, the former, which is an aldehydo-acid, is attacked. (4) Santonin is converted by potassium hydroxide, in the light, into photosantonic and photosantoninic acids, the proportion of the latter formed increasing with the amount of alkali employed. A tabular *résumé* of the behaviour of santonin and its derivatives towards potassium hydroxide in the dark and in the light and towards hydrochloric acid is given.

The chemical actions of light are classified by the authors under the following headings:—(1) Stereoisomeric transformation. (2) Polymerisation. (3) Intermolecular reactions. (4) Reciprocal actions and photosynthesis. (5) Isomerisation by the displacement of ethylene linkings. Examples of these different actions are quoted.

The formation of photosantoninic acid is assumed to be due to the reciprocal action of santoninic acid and nascent photosantonic acid, but the mode of combination is as yet unknown. T. H. P.

Identity of Stenhouse's Larixinic Acid and Maltol. Alberto Peratoner and A. Tamburello (*Ber.*, 1903, **36**, 3407—3409).—The compound obtained by Stenhouse (this Journal, 1863, **16**, 310) from the bark of larches, and described as larixinic acid, $C_{10}H_{10}O_5$, is now shown to be identical with Brand's (Abstr., 1894, i, 270) and Kiliani's (*ibid.*, 1895, i, 164) maltol. It melts at 159° and yields a benzoyl derivative melting at 115°. J. J. S.

Hexahydrobenzaldehyde, Hexahydroacetophenone, and the corresponding Secondary Alcohol. Louis Bouveault (*Bull. Soc. chim.*, 1903, [iii], **29**, 1049—1051. Compare Bouveault and Blanc, Abstr., 1903, i, 673).—*Hexahydrobenzaldehyde*, $C_6H_{11}\cdot CHO$, obtained by oxidation of the corresponding alcohol (*loc. cit.*), is a colourless liquid with a suffocating odour, recalling simultaneously that of benzaldehyde and of valeraldehyde; it boils at 159° and has a sp. gr. 0·945 at 0°/4°. The *sodium bisulphite* compound is crystalline and somewhat soluble in water. The *semicarbazone* is crystalline, melts at

176°, is readily soluble in alcohol, less so in water, and insoluble n ether or benzene.

cyclo*Hexylmethylcarbinol*, $C_6H_{11}\cdot CHMe\cdot OH$, obtained by the action of acetaldehyde on the magnesium derivative of chloro*cyclo*hexane, is a viscid liquid with a slight odour of peppermint; it boils at 87° under 11 mm. pressure, and has a sp. gr. 0·942 at 0°/4°. It is oxidised by chromic acid in presence of sulphuric acid to *hexahydroacetophenone*, $C_6H_{11}\cdot COMe$, a colourless liquid with a pleasant odour resembling that of the aliphatic ketones of similar molecular weight; it boils at 68° under 12 mm. pressure, and has a sp. gr. 0·937 at 0°/4°. The *sodium bisulphite* compound is crystalline, and the *semicarbazone* forms fine, white lamellæ, melts at 175°, is slightly soluble in boiling water, readily so in alcohol, and insoluble in ether, benzene, or light petroleum. T. A. H.

p-Halogen-*o*-nitrobenzaldehydes. FRANZ SACHS and RICHARD KEMPF (*Ber.*, 1903, 36, 3299—3303).—When 2-nitro-4-aminobenzaldoxime is distilled with aqueous ferric chloride, a 60 per cent. yield of 4-*chloro-2-nitrobenzaldehyde* is obtained; this crystallises from dilute alcohol in long, yellowish, silky needles, melts at 67°, and can also be obtained from 2-nitro-4-aminobenzaldoxime by means of the diazo-reaction. The *phenylhydrazone*, $NO_2\cdot C_6H_3Cl\cdot CH:N_2HPh$, separates from alcohol as a dark reddish-brown, crystalline powder and melts at 180—181° (corr.). The *semicarbazone*, $C_8H_7O_3N_4Cl$, crystallises from glacial acetic acid in small, bright yellow, rectangular plates and melts at 269—270° (uncorr.). 4-*Chloro-2-nitrosobenzoic acid*, obtained by exposing the aldehyde dissolved in benzene to light, crystallises from dilute alcohol in small, white rhombohedra.

4-*Bromo-2-nitrobenzaldehyde*, obtained by diazotising 2-nitro-4-aminobenzaldoxime dissolved in hydrobromic acid and decomposing the product with copper powder, crystallises from alcohol and melts at 97—98° (corr.); the *phenylhydrazone* forms lustrous, brownish-red needles and melts at 181—182° (corr.).

4-*Iodo-2-nitrobenzaldehyde* melts at 110—111° and its *phenylhydrazone* at 185° (corr.). W. A. D.

Reaction of Ethyl α-Cyanopropionate with Benzaldehyde. LODOVICO BECCARI (*Atti R. Accad. Torino*, 1903, 38, 547—555).—The action of ethyl α-cyanopropionate (2 mols.) on benzaldehyde (1 mol.) in presence of ammonia (2 mols.) yields: (1) a small quantity of a *compound*, $C_{18}H_{17}ON_3$, separating from alcohol as a heavy, crystalline powder which melts and decomposes at 210°; (2) α-cyanopropionamide, which melts at 105—106°, and not at 85° as was stated by Henry (*Bull. Acad. Roy. Belg.*, 1889, 680); (3) a *compound*, $C_{18}H_{17}ON_3$, to which the constitution $CHPh:N\cdot CHPh\cdot CMe(CN)\cdot CO\cdot NH_2$, is ascribed; it is a neutral, unstable compound separating from alcohol in white, acicular crystals melting and decomposing at 198°, and is soluble to a slight extent in chloroform, ether, or benzene; with alkalis or dilute acids, it yields benzaldehyde and ammonia, the amount of the latter corresponding with two-thirds of the total nitrogen present. It is also obtained by the action (1) of benz-

aldehyde (2 mols.) on α-cyanopropionamide (1 mol.) in presence of aqueous or, better, alcoholic ammonia and (2) of α-cyanopropionamide (1 mol.) or hydrobenzamide (1 mol.) in alcoholic solution. The *ester*, $CHPh\colon N\cdot CHPh\cdot CMe(CN)\cdot CO_2Et$, corresponding with the above amide, is obtained by the interaction of ethyl α-cyanopropionate and hydrobenzamide, and separates from alcohol in crystals which melt and decompose at 195° and are insoluble in water. T. H. P.

o-Tolualdehyde. H. Fournier (*Compt. rend.*, 1903, **137**, 716—717).—Potassium dichromate and sulphuric acid oxidise *o*-tolylcarbinol, prepared by Tiffeneau and Delange's method (this vol., i, 48), to *o*-tolualdehyde, boiling at 90° (corr.) under 20 mm. pressure and at 197° under the ordinary pressure. The semicarbazide melts at 209°, and the *semicarbazide* of *p*-tolualdehyde at 215°. Phenylbenzylhydrazine has certain advantages over semicarbazide for the character isation of aromatic aldehydes, and forms very stable crystalline derivatives. The following were prepared:

	M.p.
o-*Tolualdehydephenylbenzylhydrazone*	87°
p-*Tolualdehydephenylbenzylhydrazone*	140°
Phenylacetaldehydephenylbenzylhydrazone	83°
p-*Ethylbenzaldehydephenylbenzylhydrazone*	104°

C. H. D.

Nitrovanillin. F. Hayduck (*Ber.*, 1903, **36**, 3528).—The *m*-nitrovanillin and *o*-nitroprotocatechuic aldehyde described by the author (Abstr., 1903, i, 826) as new substances have already been prepared by Vogl (Abstr., 1899, i, 697) and by Pschorr and Sumuleanu (Abstr., 1900, i, 178) respectively. W. A. D.

The Migration of Phenyl. Marc Tiffeneau (*Compt. rend.*, 1903, **137**, 989—991. Compare Abstr., 1902, i, 666).—The compound obtained by the action of magnesium phenyl bromide on chloroacetone is decomposed by gentle heat, forming benzyl methyl ketone, $CH_2Ph\cdot CO\cdot CH_3$. When the phenyl group is at a distance from the chlorohydrin group in the original compound, no migration of the phenyl takes place, but aldehydes are formed. It is concluded that in the passage from an ethylene oxide to an aldehyde or ketone, phenyl is more mobile than hydrogen, and hydrogen more mobile than alkyl groups. C. H. D.

Condensation of Carbon Tetrachloride with Chlorobenzene by means of the Friedel and Crafts Reaction. James F. Norris and W. C. Twieg (*Amer. Chem. J.*, 1903, **30**, 392—399).—It has been shown by Norris and Green (Abstr., 1902, i, 379) that chlorobenzene reacts with carbon tetrachloride in presence of aluminium chloride with the formation of a dichlorobenzophenone chloride. It is now found that the product consists of a mixture of the chlorides of 4 : 4′- and 2 : 4′-dichlorobenzophenones, which were separated by conversion into the corresponding ketones.

When *o*-chlorobenzoic chloride is treated with chlorobenzene and

aluminium chloride, it is converted into 2 : 4′-*dichlorobenzophenone*, which crystallises in colourless prisms, melts at 66·5—67°, and is identical with the ketone of lower melting point obtained from carbon tetrachloride. By the action of phosphorus pentachloride on this ketone, 2 : 4′-*dichlorobenzophenone chloride* is obtained as an oil which boils at 223° under 23 mm. pressure.

4 : 4′-*Dichlorobenzophenone chloride* crystallises in prisms, melts at 52—53°, boils at 223° under 18 mm. pressure, and is readily soluble in light petroleum.

A study has been made of the best conditions for the condensation of carbon tetrachloride with *p*-dichlorobenzene, as a result of which an improved method is described for the preparation of 2 : 5 : 2 : 5′-tetrachlorobenzophenone chloride. E. G.

Synthesis of Dihalogen Derivatives of Benzophenone. F. Bodroux (*Compt. rend.*, 1903, **137**, 710—712).—*p*-Chloro- and *p*-bromo-phenyl magnesium bromides react in ethereal solution with carbon dioxide, forming a halogen-benzoic acid and a di-derivative of benzophenone, the latter compound predominating at the boiling point of ether and the former at low temperatures. C. H. D.

Synthesis of a Benzoyl-*m*-xylenol. Adolfo Linari (*Gazzetta*, 1903, **33**, ii, 60—65. Compare Bartolotti and Linari, Abstr., 1902, i, 792; 1903, i, 177).—*Benzoyl*-1 : 3 : 4-*xylenol*, $C_6H_2BzMe_2·OH$, was prepared by the action of benzoyl chloride, in presence of sodium hydroxide, on 1 : 3 : 4-xylenol, and was purified by conversion into the *benzoyl* compound, $C_6H_2BzMe_2·OBz$, by the action of benzoyl chloride and zinc chloride in chloroform solution, and subsequent treatment of this product with alcoholic sodium hydroxide. It crystallises from alcohol in shining, white scales melting at 145—146° and dissolves slightly in alkali hydroxide solutions, to which it imparts a yellow colour. Its *methyl* derivative, $C_6H_2BzMe_2·OMe$, separates from alcohol in large, colourless prisms melting at 52·5—53·5°, and its *dibromo*-derivative, $C_6Br_2BzMe_2·OH$, is deposited from aqueous alcohol in mammellary masses of colourless crystals melting at 161—162°.

T. H. P.

Condensation Products of Dibenzyl Ketone and Benzaldehyde. Guido Goldschmiedt and Karl Spitzauer (*Monatsh.*, 1903, **24**, 720—728. Compare Abstr., 1899, i, 140; 1900, i, 35; Stoermer and Wehln, Abstr., 1903, i, 40).—αβδε-Tetraphenylpentane-γ-one-αε-diol forms a *diacetate*, $CO(CHPh·CHPh·OAc)_2$, which crystallises in delicate, white needles and melts at 180—181°, and a *dibenzoate*, which crystallises in glistening, white needles and melts at 136°. αβδ-Triphenylbutane-γ-one-α-ol forms an *acetate*,

$$OAc·CHPh·CHPh·CO·CH_2Ph,$$

which crystallises in clusters of needles and melts at 109—111°, and a *benzoate*, which melts at 147—149°.

The action of hydrogen chloride on a mixture of dibenzyl ketone and benzaldehyde leads to the formation of benzylidenedibenzyl

ketone, which melts at 163° and is obtained instead of 1 : 2-diphenyltetrahydro-β-naphthenone by the action of potassium hydroxide on its additive compound with hydrogen chloride. In one experiment, the action of hydrogen chloride lead to the formation of an isomeric ketone, $C_{22}H_{18}O$, which melts at 86° and dissolves in sulphuric acid to an emerald-green solution. G. Y.

Addition of Acids to $\alpha\beta$-Unsaturated Ketones. DANIEL VORLÄNDER and M. HAYAKAWA (*Ber.*, 1903, 36, 3528—3546. Compare Vorländer and Mumme, Abstr., 1903, i, 495).—Unsaturated ketones of the type R·CH:CH·CO·CH:CH·R give with acids two mono-additive compounds, which may be represented by the formulæ *A*, R·CH(XH):CH·COR and *B*, R·CHX·CH_2·CO·R (or R·CH_2·CHX·CO·R).
With two molecules of acid, three compounds are obtainable, to which the formulæ: 2*A*, R(HX)·CO·R(HX); 2*B*, R·HX·CO·RHX; *AB*, R(HX)·CO·RHX, are given. The compounds of the type *A* are coloured and relatively unstable; sometimes they can be isolated, but in many cases their formation is evident only from their colour, since they are readily transformed into colourless compounds of the type *B*. The acid may be regarded as combined as such in compounds of the *A* form, as it can be removed quantitatively by simply digesting the additive compound with water for several hours at the ordinary temperature, whilst for the removal of the acid, the additive compound of the *B* form requires to be heated for 4—5 hours with aqueous alcoholic sodium hydroxide.

On passing dry hydrogen bromide into cooled benzylidenepinacolin, a golden-yellow liquid is obtained, which soon solidifies to a crystalline mass; on recrystallising the product from ether, the *hydrobromide B*, $C_{13}H_{17}OBr$, separates in white needles melting at 44°. It rapidly loses hydrogen bromide when kept, and is reconverted into benzylidenepinacolin; it is thus similar to the hydrochloride already described (*loc. cit.*).

Phorone gives only additive compounds of the *B* type; the *dihydrobromide B*, $C_{19}H_{14}O,2HBr$, prepared by passing hydrogen bromide through phorone at 0°, forms white plates melting at 19°; the *dihydrochloride B* can only be obtained as a liquid which loses acid only very slowly when shaken with water; when distilled four times, however, it is completely reconverted into phorone.

The *monohydrobromide A* of dibenzylideneacetone separates in small, orange-coloured needles on first passing hydrogen bromide into a solution of the ketone in dry benzene or light petroleum; it becomes orange-red at 95°, melts at 100°, and decomposes at 115°; if an excess of hydrogen bromide is used, the *dihydrobromide 2A* is obtained in red crystals, which are very unstable, and are immediately and completely decomposed by cold water giving dibenzylideneacetone. When the dihydrobromide A is exposed to moist air or kept in a desiccator over soda-lime, it regenerates the monohydrobromide A. The *dihydrobromide 2B* is prepared by passing hydrogen bromide through a solution of dibenzylideneacetone in light petroleum for 4 hours, when most of the coloured hydrobromide which first separates redissolves;

on evaporating the solution and crystallising the product from ether or glacial acetic acid, white leaflets are obtained, which become orange at 65—73° and melt and decompose at 124—126°. The same substance is obtained when hydrogen bromide is passed over dry benzylideneacetone for 8 hours; hydrogen chloride, however, under the same conditions, gives rise almost exclusively to the orange dihydrochloride 2*A* (compare *loc. cit.*).

The *monohydrobromide A* of dianisylideneacetone is obtained as a brown precipitate on passing hydrogen bromide into a solution of the ketone in benzene; it melts and decomposes at 165°, and is easily converted by an excess of the acid into the violet *dihydrobromide 2A*; with a great excess of sulphuric acid (100 mols.), anisylideneacetone combines to form a crystalline, reddish-violet *dihydrosulphate*, $C_{19}H_{18}O_3,2H_2SO_4$.

Dicinnamylidene*cyclo*pentanone combines with hydrogen bromide to form a black *dihydrobromide 2A*. With bromine (1 mol.) in ice-cold chloroform solution, dicuminylideneacetone yields a *dibromide*, $C_{23}H_{26}OBr_2$, which separates from ether in white crystals, melts at about 110°, and decomposes at 138°; with 2 mols. of bromine, the *tetrabromide*, $C_{23}H_{26}OBr_4$, is obtained, which forms white needles and melts at 189°. W. A. D.

Benzoylfluorene. GUSTAVE PERRIER (*Monatsh.*, 1903, **24**, 591—592). GUIDO GOLDSCHMIEDT (*ibid.*, 592—594. Compare Fortner, Abstr., 1903, i, 177).—A question of priority. Perrier has previously described (*Thèse inaugrale*, Paris, 1896) the preparation of benzoylfluorene (m. p. 123°), its oxime (m. p. 208°), and the corresponding secondary alcohol (m. p. 113°). G. Y.

Aromatic Hydroxy-ketones. KARL AUWERS (*Ber.*, 1903, **36**, 3890—3892).—The following compounds were prepared by condensing phenetole and *p*-tolyl ethyl ether by means of aluminium chloride with various acid chlorides and hydrolysing the ethers so obtained by Hartmann and Gattermann's method (Abstr., 1893, i, 152).

p-*Hydroxy*-i-*valerophenone*, $OH·C_6H_4·CO·C_4H_9$, crystallises from ether in rhombic prisms and melts at 97—98°. p-*Hydroxypalmitophenone*, $OH·C_6H_4·CO·C_{15}H_{31}$, separates from light petroleum in slender needles melting at 78°. 3′-*Nitro*-4-*hydroxybenzophenone* forms yellow prisms, melts at 173°, and gives an *ethyl ether* which crystallises from a mixture of absolute alcohol and light petroleum in slender, white prisms and melts at 79—81°. 1′-*Nitro*-4-*hydroxybenzophenone* was not obtained pure; its *ethyl ether* crystallises from alcohol in dark yellow prisms melting at 115°. 6-*Hydroxy*-3-*methylpropiophenone*, $OH·C_6H_3Me·CO·C_2H_5$, melts at −2° and boils at 135—140° under 22 mm. pressure. 6-*Hydroxy*-3-*methyl*-n-*butyrophenone* crystallises from dilute alcohol in slender, rhombic prisms, melts at 34°, and gives an *ethyl ether* which boils at 205° under 100 mm. pressure. 6-*Hydroxy*-3-*methylbenzophenone* forms yellow leaflets melting at 84°, and its *ethyl ether* forms yellow needles and melts at 68°. 4′-*Nitro*-6-*hydroxy*-3-*methylbenzophenone* crystallises from alcohol in thin, yellow plates and melts at 142—143°. W. A. D.

Preparation and Hydrolysis of Phenol Ethers by Gattermann's Method. KARL AUWERS (*Ber.*, 1903, **36**, 3893—3902).—When *p*-nitrobenzoyl chloride is condensed with phenetole in carbon disulphide solution by means of aluminium chloride, 4′-nitro-4-ethoxybenzophenone, melting at 112°, is the principal product, but 4′-*nitro-2-hydroxybenzophenone* is also always formed, together with traces of 4′-*nitro-4-hydroxybenzophenone*; it is probable that the former of these phenols owes its origin to the hydrolysis by aluminium chloride of the corresponding ether, formed simultaneously with 4′-nitro-4-ethoxybenzophenone, although this could not be isolated. An alternative explanation would be the wandering of the radicle $NO_2\cdot C_6H_4\cdot CO\cdot$ from the para- into the ortho-position relatively to the hydroxyl, but there is little evidence to favour such an assumption.

4′-*Nitro-2-hydroxybenzophenone* crystallises in slender, yellow prisms and melts at 111—113°. 4′-*Nitro-4-hydroxybenzophenone*, prepared by hydrolysing its ethyl ether by means of aluminium chloride in carbon bisulphide solution, crystallises in slender, yellow needles, and after softening at 182° melts at 190—192°; in this hydrolysis, not a trace of the isomeric 4′-nitro-2-hydroxy-compound is formed. 4′-*Nitro-4-acetoxybenzophenone* crystallises from alcohol in long needles and melts at 131°.

When anisole is condensed with *p*-nitrobenzoyl chloride under the foregoing conditions, the principal product is 4′-*nitro-4-methoxybenzophenone*, which crystallises from alcohol or glacial acetic acid in white needles, melts at 121°, and on hydrolysis behaves normally, giving 4′-nitro-4-hydroxybenzophenone only.

The constitution of 4′-nitro-4-hydroxybenzophenone was established by reducing it to the corresponding amino-derivative and converting this into 4 : 4′-dihydroxybenzophenone. From 4′-nitro-4-methoxybenzophenone, in a similar manner, 4′-*hydroxy-4-methoxybenzophenone* was obtained; it crystallises from hot water or toluene in lustrous needles, melts at 151—152°, and on methylation gives 4 : 4′-dimethoxybenzophenone (Bösler, Abstr., 1881, 421).

4′-*Nitro-2-methoxybenzophenone*, prepared by methylating the phenol melting at 111—113°, crystallises from alcohol or light petroleum in lustrous, flat prisms or plates and melts at 117—119°. 4′:2-Dihydroxybenzophenone was obtained from the same substance by reduction and subsequent diazotisation, thus proving the structure of the phenol.

W. A. D.

Transformation of Acetophenone *O*-Benzoate into Dibenzoylmethane. LUDWIG CLAISEN and EMIL HAASE [and, in part, with A. BEHRE] (*Ber.*, 1903, **36**, 3674—3682. Compare Abstr., 1897, i, 188).—Lee's *O*-benzoylated acetophenone [α-benzoxy-α-phenylethylene] (Trans., 1903, **83**, 145) has been obtained in the form of crystals melting at 41°.

When a mixture of acetophenone, benzoyl chloride, and pyridine is left for 6—7 weeks at the ordinary temperature, a compound, $C_{20}H_{17}O_2N$, is obtained. It crystallises in small, yellow prisms, melts at 110°, and decomposes above 230°. When hydrolysed, it yields acetophenone, benzoic acid, and pyridine.

Dibenzoylmethane, in the form of its sodium derivative, may be

obtained by warming a benzene solution of the *O*-benzoyl derivative with sodium wire and a small amount of sodioacetophenone. To obtain dibenzoylmethane itself, the mass is extracted with water and the aqueous solution decomposed by carbon dioxide. The mechanism of the reaction is probably first the addition of the *O*-benzoylacetophenone molecule to sodioacetophenone, yielding the compound

$$ONa{\cdot}CPh(O{\cdot}CPh{:}CH_2)_2,$$

which then becomes transformed into

$$ONa{\cdot}CPh(CH_2{\cdot}COPh){\cdot}O{\cdot}CPh{:}CH_2,$$

and this, by the loss of a molecule of acetophenone, yields

$$ONa{\cdot}CPh{:}CH{\cdot}COPh.$$

When dibenzoylmethane is benzoylated by the aid of benzoyl chloride and pyridine, it yields an O-*benzoyl* derivative, $OBz{\cdot}CPh{:}CHBz$, melting at 108—109°. When this is heated for several hours at 230—240°, it yields benzoic acid and a compound, $C_{15}H_{10}O$, melting at 225—230° and insoluble in acetone.

A summary of the modes of formation and properties of the various benzoyl derivatives of methane is given. J. J. S.

[Dinitrophenyl Ether of Quinoneoxime.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 144765).—When nitrosophenol is heated in alcoholic solution with a molecular proportion of 1-chloro-2 : 4-dinitrobenzene in presence of sodium acetate or carbonate, condensation takes place to *quinoneoxime dinitrophenyl ether*, $O{:}C_6H_4{:}N{\cdot}O{\cdot}C_6H_3(NO_2)_2$, a crystalline compound melting and decomposing at 165°, insoluble in dilute acids or alkalis. Gentle reducing agents, as sodium sulphide, form *p*-aminophenol and 2 : 4-dinitrophenol. Fusion with sulphur and sodium sulphide converts it into a black dye. C. H. D.

o-Methoxyanthraquinonesulphonic Acids. FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 145188).—*Sodium*-1-*methoxyanthraquinone*-6-*sulphonate*, $NaSO_3{\cdot}C_6H_3{<}^{CO}_{CO}{>}C_6H_3{\cdot}OMe$, prepared by heating together sodium α-nitroanthraquinonesulphonate, sodium hydroxide, methyl alcohol, and water in a reflux apparatus, is a yellowish-brown, crystalline powder, dissolving in water. When heated with sulphuric acid at 120°, it is hydrolysed, forming 1-hydroxyanthraquinone-6-sulphonic acid. The sodium salt of this acid, when heated with calcium hydroxide under pressure, forms 1 : 6-*dihydroxyanthraquinone*, crystallising from dilute alcohol in large, yellow needles melting at 260° and dissolving in concentrated sulphuric acid and dilute alkalis to yellowish-red solutions. The constitution follows from the fact that all the other dihydroxyanthraquinones are known, and is confirmed by the oxidation of α-aminoanthraquinonesulphonic acid by potassium permanganate to 1 : 2 : 4-sulphophthalic acid, proving that the sulpho- and methoxy-groups are in different rings.

When β-nitroanthraquinonesulphonic acid is treated in this way, *sodium* 1-*methoxyanthraquinone*-7-*sulphonate* is obtained as a yellowish-brown powder. When heated with lime under pressure, *m*-benzdihydroxyanthraquinone is formed. β-Aminoanthraquinonesulphonic acid is oxidised to the same sulphophthalic acid as the α-compound.

C. H. D

New Anthracene Dyes. PAUL FRIEDLÄNDER and G. SCHICK (*Zeit. Farb. Text. Chem.*, 1903, 2, 429—430).—Alizarincyanin-green, when reduced with stannous chloride, gives dihydroquinizarin, *p*-toluidine, and *p*-toluidinesulphonic acid; it therefore has the constitution of a *di*-p-*toluidinoanthraquinonesulphonic acid*,

$$[NH{\cdot}C_6H_4Me : NH{\cdot}C_6H_3Me{\cdot}SO_3H = 1 : 4].$$

Alizarinirisol is similarly shown to be 4-*hydroxyanthraquinone*-1-p-*toluidinosulphonic acid* $[NH{\cdot}C_6H_3Me{\cdot}SO_3H : OH = 1 : 4]$. When heated with 60 per cent. sulphuric acid, it is converted into an *acridine* derivative,

$$C_6H_3Me{<}\genfrac{}{}{0pt}{}{N - C_6H_2(OH)}{C - - - - C_6H_4}{>}CO,$$

which crystallises from glacial acetic acid in brownish-black leaflets and is strongly fluorescent. W. A. D.

Nitro-derivatives of Phenanthraquinone. JULIUS SCHMIDT (*Ber.*, 1903, 36, 3726—3730).—A summary of the principal results contained in the four following papers. C. H. D.

The Phenanthrene Series. VII. 2-Nitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and PATRIC C. AUSTIN (*Ber.*, 1903, 36, 3730—3734).—2-Nitrophenanthraquinone is best prepared by boiling phenanthraquinone with concentrated nitric acid for 2 minutes and immediately pouring into cold water. On crystallising from glacial acetic acid, the 2-nitro-compound separates first, and the mother liquor deposits, on evaporation, the 4-nitro-compound (see following abstract).

2-*Nitrophenanthraquinoneoxime* forms greenish-yellow needles which melt and decompose at 213°, softening previously. 2-*Nitro*-9 : 10-*dihydroxyphenanthrene*, prepared by reduction of the quinone, forms small, brownish-yellow crystals, decomposing slowly on heating and then melting at about 220°; it dissolves in dilute aqueous sodium hydroxide to a brownish-violet solution. Even traces give a reddish-violet solution in concentrated sulphuric acid. The *diacetyl* derivative forms bright yellow needles softening at 250° and melting at 258°. The quinone is oxidised by heating with a mixture of concentrated sulphuric acid and potassium dichromate to p-*nitrodiphenic acid*, crystallising from water in glistening, white leaflets melting at 214—216° and dissolving readily in alcohol or ether, less readily in hot water or benzene. Tin and hydrochloric acid reduce it to p-*aminodiphenic acid*, crystallising from water, and melting and decomposing at 277°.

3-Nitrophenanthraquinone (Schmidt and Kämpf, Abstr., 1902, i, 797) is oxidised to m-*nitrodiphenic acid*, crystallising from water in white, silvery leaflets melting at 268°. C. H. D.

The Phenanthrene Series. VIII. 4-Nitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ADOLF KÄMPF (*Ber.*, 1903, 36, 3734—3738).—4-*Nitrophenanthraquinone* has not been previously prepared, the substance obtained by Kehrmann and Kikine (Abstr., 1900, i, 61) being a mixture containing 4 : 5-dinitrophenanthraquinone. Prepared as described in the preceding abstract, it

forms bright yellow groups of needles melting at 179—180° after repeated recrystallisation from alcohol. When precipitated from sulphuric acid solution by water, it dissolves in dilute alkali hydroxides to a yellow solution, from which it is precipitated unaltered by acids. Its constitution is proved by its ready conversion by boiling with fuming nitric acid into 4 : 5-dinitrophenanthraquinone (see following abstracts). The *oxime* crystallises from alcohol in greenish-yellow needles melting at 169—170°. The cold alcoholic solution is coloured dark reddish-brown by ferric chloride. On boiling an alcoholic solution of the quinone with *o*-phenylenediamine hydrochloride, o-*nitrodiphenylenequinoxaline*, $C_6H_4<\begin{matrix} N:C\cdot C_6H_4 \\ N:C\cdot C_6H_3\cdot NO_2 \end{matrix}$, is formed, crystallising from benzene in hair-like needles melting at 217—218°. Hydrogen sulphide or phenylhydrazine readily reduces the quinone to the quinol, which is unstable, but may be converted into the acetyl derivative by boiling with acetic anhydride. 4-*Nitro*-9 : 10-*diacetoxyphenanthrene* crystallises from 60 per cent. acetic acid in white needles melting and decomposing at 222—223°.

4-Nitrophenanthraquinone may be oxidised by chromic acid in the same way as the 2-nitro-compound, forming o-*nitrodiphenic acid*, crystallising from 30 per cent. acetic acid in large, white leaflets melting and decomposing at 248—250°, dissolving readily in alcohol, ether, acetone, or glacial acetic acid, sparingly in benzene, chloroform, or light petroleum. The salts of the alkaline earth metals are soluble, those of lead and silver insoluble. Unlike the dinitrodiphenic acids, the acid has no bitter taste. Tin and hydrochloric acid reduce it to o-*aminodiphenic acid*, which forms white needles, very sparingly soluble in water and remaining unmelted at 300°. C. H. D.

The Phenanthrene Series. IX. 2 : 7-Dinitrophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ADOLF KÄMPF (*Ber.*, 1903, **36**, 3738—3744).—2 : 7-Dinitrophenanthraquinone (Abstr., 1902, i, 797) forms an *oxime*, which crystallises in slender, yellow needles melting at 246—248°, at the same time becoming green and evolving gas. 4 : 4'-*Dinitrodiphenylenequinoxaline* crystallises from benzene in almost white needles melting at 356°. Alcoholic ammonia converts the quinone into 2 : 7-*dinitrophenanthraquinoneimide*, crystallising from alcohol in brownish-yellow needles melting and decomposing at 358—360°. 2 : 7-*Dihydroxyphenanthraquinone*, prepared by boiling the diazonium compound of 2 : 7-diaminophenanthraquinone (compare Anschütz and Meyer, Abstr., 1885, 1067), is a dark brownish-red powder melting above 400° and dissolving readily in alcohol, acetone, or glacial acetic acid to reddish-violet solutions, less readily in ether or ethyl acetate, very sparingly in benzene. Alkali hydroxides dissolve it to a green solution, from which carbon dioxide again precipitates it. The solution in concentrated sulphuric acid is greenish-brown, giving a black precipitate with potassium dichromate, again dissolving on addition of more dichromate. The *diacetyl* derivative crystallises from glacial acetic acid in glistening red tablets, melting and decomposing at 235—236°.

An attempt to synthesise the dinitroquinone from 4 : 4′-dinitrodiphenic acid was made. 4 : 4′-*Dinitrodiphenic chloride* separates from benzene in white crystals melting at 138°. Heating with copper powder at 265° produced no condensation ; at 290°, explosive decomposition occurred. The presence of the two nitro-groups appears to cause mutual repulsion of the carboxyl groups, thus hindering the anhydride formation. C. H. D.

The Phenanthrene Series. X. 4 : 5-Dinitrophenanthraquinone and its Derivatives. Julius Schmidt and Adolf Kämpf (*Ber.*, 1903, **36**, 3745—3752).—4 : 5-Dinitrophenanthraquinone, obtained in the preparation of the 2 : 7-isomeride, melts after repeated treatment with hot fuming nitric acid at 228°. Chromic acid oxidises it to 2 : 2′-dinitrodiphenic acid (compare Schultz, Abstr., 1880, 814), which is well suited to its identification. Anhydride formation does not take place. When mixed with sand and distilled at 300° under 30 mm. pressure, 2 : 2′-dinitrodiphenyl is produced, together with a small quantity of a sparingly soluble compound melting at 240°, probably dinitrofluorenone.

2 : 2′-*Diaminodiphenic acid*, prepared by reduction of the dinitro-acid with tin and fuming hydrochloric acid, is very insoluble in water. When mixed with barium hydroxide and distilled, carbazole is produced, thus confirming the constitution assigned to the dinitro-compound.

4 : 5-*Dinitrophenanthraquinoneoxime* crystallises from alcohol in yellow clusters, melting and decomposing at 190—191°. 2 : 2′-*Dinitrodiphenylenequinoxaline* forms pale red needles melting at 262—264°. When the quinone is heated with fuming sulphuric acid on the water-bath, no sulphonic acid is formed, but 2 : 2′-dinitrodiphenic acid is obtained, the reaction thus resembling the oxidation of naphthalene to phthalic acid.

4 : 5-*Dinitro*-9 : 10-*diacetoxyphenanthrene*, which forms white needles, melts at 258°, the *dibenzoyl* derivative melts at 210°.

Tin and fuming hydrochloric acid reduce the dinitroquinone to 4 : 5-*diamino*-9 : 10-*dihydroxyphenanthrene*, which is unstable, its *hydrochloride* forms large, white needles which darken superficially on drying. On adding an excess of potassium carbonate to the solution and passing a current of air, 4 : 5-*diaminophenanthraquinone* is precipitated in black flocks, and may be obtained in indefinite crystals, melting at about 235°, by solution in alcohol. Attempts to obtain intramolecular condensation, or combination, with α-diketones were unsuccessful. 4 : 5-*Dihydroxyphenanthraquinone* forms dark red crystals charring at 400° without previous fusion. It is more readily soluble in organic solvents than the 2 : 7-derivative. The solution in concentrated sulphuric acid is brownish-red, giving no characteristic reaction with potassium dichromate. 4 : 5-*Dimethoxyphenanthraquinone* separates from dry ether in dark red crystals melting at 190—191° after softening, dissolving readily in benzene or glacial acetic acid, less readily in ethyl or methyl alcohol. The *dibenzoyl* derivative crystallises from alcohol in slender, yellow needles melting at about 170°. C. H. D.

Interaction of Mercuric Acetate with Terpenes and Compounds containing the C_3H_5 Group. II. LUIGI BALBIANO and VINCENZO PAOLINI (*Ber.*, 1903, 36, 3575—3584. Compare Abstr., 1902, i, 808).—The compound, $C_{10}H_{16}O_2$, prepared by the action of mercuric acetate on pinene is converted into carvacrol by warming with dilute sulphuric acid, thus proving the position of the hydroxyl-group, whilst its oxidation to terpenylic acid proves the position of the carbonyl group; it is therefore a *6-hydroxy-Δ^6-menthen-2-one*, $CH_3\cdot C\Big<\begin{matrix}C(OH)\cdot CH_2\\ CO——CH_2\end{matrix}\Big>CH\cdot CHMe_2$, and a hydroxy-derivative of Harries' menthenone (Abstr., 1901, i, 551), but it could not be reduced.

[With GION VESPIGNANI.]—The same compound is produced from *d*-pinene.

Camphene yields a *compound*, $C_{10}H_{16}O(Hg\cdot OAc)_2$, which crystallises in glistening, white, odourless flakes and melts at 188—189°; hydrogen sulphide reconverts it into camphene, and this is also formed on attempting to reduce it with sodium amalgam or with zinc and potassium hydroxide. The *mercurichloride*, $C_{10}H_{16}O(HgCl)_2$, is a white, odourless powder, insoluble in neutral solvents, and softens at 150°, but does not melt at 250°.

Pinene thus behaves as a propenyl, and camphene as an allyl compound, in accordance with the formulæ $CH\Big\langle\begin{matrix}\!\!/\!\!/CMe\cdot CH-\\ CMe_2\\ CH_2-CH-\end{matrix}\Big\rangle CH_2$ and $\begin{matrix}CH_2\cdot CH\cdot CMe_2\\ |\quad CH_2\quad |\\ CH_2\cdot CH\cdot C\colon CH_2\end{matrix}$, since the propenyl compounds are oxidised by mercuric acetate, whilst allyl compounds yield additive products. Thus, on covering a saturated solution of mercuric acetate with benzene containing two or three drops of a propenyl compound such as anethole, methyl*iso*eugenol, or *iso*safrole, mercurous acetate separates in 15 to 45 minutes, whilst with an allyl compound such as methylchavicol, methyleugenol, or safrole, the two layers remain clear for two or three days; apiole gives an immediate precipitate of the insoluble additive compound, but this in no way resembles the characteristic flakes of mercurous acetate. The additive products have the general formula $R\cdot C_3H_5(OH)\cdot Hg\cdot OAc$, and are mixtures of two isomerides which can sometimes be separated by conversion into the corresponding chlorides, but cannot usually be reduced to the hydroxypropyl compounds, $R\cdot C_3H_6\cdot OH$, as these are unstable and readily lose a molecule of water.

[With ENRICO LUZZI.]—Safrole yields the crystalline *additive compound*, $CH_2\colon O_2\colon C_6H_3\cdot C_3H_5(OH)\cdot Hg\cdot OAc$, which is converted by sodium chloride into the *mercurichloride*, $CH_2\colon O_2\colon C_6H_3\cdot C_3H_5(OH)\cdot HgCl$, a white, crystalline powder, insoluble in water and sparingly soluble in boiling alcohol, which blackens and decomposes at 170°, and is reduced by zinc and sodium hydroxide to safrole. The syrupy, isomeric mercuriacetate yields a *mercurichloride* which crystallises from alcohol in rosettes of hard, glistening, prismatic needles, melts at 138°, and

solidifies to a glassy mass, and is reduced to safrole by zinc and sodium hydroxide. *iso*Safrole reduces the mercuric to mercurous acetate and is oxidised to the glycol, $CH_2{:}O_2{:}C_6H_3{\cdot}C_3H_5(OH)_2$, which crystallises in stout crystals and melts at 101—102° (Wagner and Bouschmakin, Abstr., 1892, 310); prolonged oxidation in warm weather yields a yellow, aromatic liquid, $C_{10}H_{10}O_3$, which boils at 142° under 23 mm. pressure; its *oxime* crystallises in needles and melts at 89°, and its *semicarbazone* crystallises in colourless flakes and melts at 158°.

[With U. Tonazzi.]—Methylchavicole, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CH_2$, an allyl isomeride of anethole, obtained from Dracuncuti oil, boils at 214—216°, and has n_D 1·5244 at 15°. The mixture of *mercuri-acetates* forms a thick syrup, of which a part becomes crystalline after some months and is separated by conversion into the corresponding chlorides and bromides. The chief *mercurichloride* is insoluble in water but dissolves in alcohol, and crystallises in white, glistening needles and melts at 81—82°; the *isomeride,* a resinous mass insoluble in alcohol, gradually hardens, and when heated, softens at 55° without showing a definite melting point; both are reduced to methylchavicole. The *mercuribromide* crystallises in white needles, melts at 70°, and is also accompanied by a resinous isomeride.

[With F. Bernardini.]—Methyleugenole forms a syrupy *mercuri-acetate*, $C_6H_3(OMe)_2{\cdot}C_3H_5(OH){\cdot}Hg{\cdot}OAc$, which gradually solidifies to a mass of radiating needles. The crystalline *mercurichloride* forms small, hard, colourless prisms, is insoluble in water, but soluble in alcohol and melts at 112—113°; the resinous isomeride was not examined, but both are reduced to methyleugenole. Methyl *iso*eugenole yields the *glycol*, $(OMe)_2C_6H_3{\cdot}C_3H_5(OH)_2$, which forms prismatic plates and melts at 120—121°; the *bisphenylcarbamide* crystallises from boiling alcohol in colourless needles and melts at 166—168°. An isomeric *glycol* is also produced which crystallises from ether in glistening prisms and melts at 88—89° (compare Kolokoloff, *J. Russ. Phys. Chem. Soc.*, 1897, **29**, 23).

[With G. Mammola.]—*Apiole mercuriacetate*,

$$CH_2{:}O_2{:}C_6H(OMe){\cdot}C_3H_5(OH){\cdot}Hg{\cdot}OAc,$$

crystallises from alcohol in minute needles and melts at 157—158°. It is reduced by zinc and sodium hydroxide to the *compound*, $CH_2{:}O_2{:}C_6H(OMe)_2{\cdot}C_3H_6{\cdot}OH$, which crystallises in glistening needles and melts at 29·5—30·5°; the *benzoyl* derivative is a viscous liquid which boils at 165° under 4 mm. pressure, and solidifies when cooled with ice to a mass of needle-shaped crystals, but again melts at ordinary temperatures. iso*Apioleglycol*, $CH_2{:}O_2{:}C_6H(OMe)_2{\cdot}C_3H_5(OH)_2$, prepared by the action of mercuric acetate on *iso*apiole, crystallises from ether in colourless needles and melts at 120°; it combines with phenylcarbimide and with benzoyl chloride, but the products were not purified. It also combines with mercuric acetate to form the *compound*, $CH_2{:}O_2{:}C_6(OMe)_2[C_3H_5(OH)_2]{\cdot}Hg{\cdot}OAc,OAcHg$, which crystallises in colourless flakes, softens at 160°, and melts and decomposes at 174°.

T. M. L.

Pulegone Nitrosite. Paul Genvresse (*Compt. rend.*, 1903, **137**, 494—495).—*Pulegone nitrosite*, $C_{10}H_{16}O_4N_2$, prepared by the action

of nitrogen peroxide, or "nitrous fumes," on a well-cooled solution of pulegone in light petroleum, crystallises in colourless, silky needles, melts at 68—69°, is soluble in cold alcohol, more so in chloroform, slightly volatile in steam, and has $[\alpha]_D + 23\cdot13°$ in chloroform at 23°. The nitrosite gives with phenol and sulphuric acid a brilliant emerald-green coloration, does not decolorise bromine, and furnishes an oily *oxime*, but does not react with piperidine or benzylamine.

T. A. H.

Terpenes and Ethereal Oils. Pulenone [1 : 4 : 4-Trimethyl-5-hexanone]. OTTO WALLACH [with WILHELM KEMPE and, in part, FRITZ COLLMANN, J. MEYER, and H. SONNEBORN] (*Annalen*, 1903, **329**, 82—108).—Pulegenic acid, which has a five-membered ring (Abstr., 1903, i, 569), is readily converted by oxidation to a hydroxy-lactone, and by subsequent treatment with sulphuric acid into a cyclic ketone, pulenone, which has now been shown to be a trimethylhexanone, $CMe_2<\begin{matrix}CH_2-CO\\CH_2\cdot CH_2\end{matrix}>CHMe$. Under the influence of the sulphuric acid, the five-membered ring in the lactone of pulegenic acid is broken, carbon dioxide eliminated, and a six-membered ring formed.

Pulenone is best prepared from pulegenic acid (Abstr., 1898, i, 484) as follows: the acid is converted into the hydroxy-lactone (m. p. 129—130°) by oxidising a dilute alkaline solution with 4 per cent. permanganate; the hydroxy-lactone is then distilled under reduced pressure with sulphuric acid, when carbon dioxide is evolved at 80° and the pulenone passes over; the ketone boils at 183°, has a sp. gr. 0 8925 and n_D 1·44506 at 21°.

Pulenol, $C_9H_{17}\cdot OH$, is prepared by reducing the ketone by sodium in moist ether, and boils at 187—189°, and has sp. gr. 0·8955 and n_D 1·4569 at 20°. With phenylcarbimide, it forms a *urethane*, $C_9H_{17}\cdot O\cdot CO\cdot NHPh$, which melts at 84—85° or 92°.

Pulenene, C_9H_{16}, is prepared by heating pulenol with potassium hydrogen sulphate at 150°, and distilling the product in steam; it is an isomeride of pulegene, and is an oil boiling at 60—65° under 12 mm. pressure; the *additive* product with nitrosyl chloride is prepared by adding a solution of the hydrocarbon and amyl nitrite in acetic acid to a cold solution of hydrogen chloride in acetic acid and forms colourless crystals melting at 98—99°. When pulenol is heated with zinc chloride at 160—170°, a *hydrocarbon* boiling at 145—150° under ordinary pressure is obtained; it yields no solid nitrosochloride.

When pulenone is oxidised with permanganate, acetic acid is formed together with a non-volatile ketonic acid, which melts at 115°, and *as*-dimethylsuccinic acid (m. p. 140°). If the oxidation is carried out with chromic acid in sulphuric acid solution, three acids are formed: a *ketonic acid*, $C_8H_{14}O_3$, melting at 49—50°, *as*-dimethylsuccinic acid, and $\alpha\alpha\delta$-trimethyladipic acid, $CO_2H\cdot CHMe\cdot[CH_2]_2\cdot CMe_2\cdot CO_2H$, which melts at 115°; when its calcium salt is distilled with soda-lime, it is converted into *trimethylpentanone*, $CMe_2<\begin{matrix}CO-CHMe\\CH_2\cdot CH_2\end{matrix}$, an oil boiling

at 152—153°; the *semicarbazone* of this cyclic ketone melts at 150—151° and the *oxime* at 60—62°. When the pentanone is oxidised by chromic acid, it is converted into the same ketonic acid (m. p. 49—50°) as is obtained by the direct oxidation of pulenone; its *semicarbazone* melts at 163°. Since it is oxidised by potassium hypobromite to αα-dimethylglutaric acid (m. p. 82°), it can only be γ-acetyl-αα-dimethylbutyric acid, $CH_2Ac\cdot CH_2\cdot CMe_2\cdot CO_2H$. Further, both pulenone and the dimethylglutaric acid yield on oxidation dimethylsuccinic acid.

By the action of phosphorous oxychloride on pulenoneoxime (which melts at 94—95° and boils at 117° under 12 mm. pressure), a feebly basic iso*oxime* is obtained; it forms crystals melting at 96—97° and boils at 145—150° under 27 mm. pressure, and cannot be converted into an amide by acids.

When boiled with acetic anhydride, pulenoneoxime loses water and yields a *nonenonitrile*, $C_8H_{15}\cdot CN$, which is an oil boiling at 89—90° under 10 mm., or at 216—217° under the ordinary pressure; it is converted into *nonenoic acid*, $CMe_2{:}CH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H$, by heating with sodium methoxide in alcoholic solution under pressure at 180°; the acid is a liquid boiling at 143—147° under 23 mm. pressure, and has a sp. gr. 0·9435 and n_D 1·4561 at 20°; its constitution is demonstrated by the fact that it is oxidised by permanganate to acetone and β-methylglutaric acid. The *iso*oxime can also be converted into this nonenoic acid by heating under pressure with sulphuric acid; the *iso*oxime consequently has the constitution $CHMe{<}\begin{matrix}CH_2\text{—}CO\text{—}NH\\ CH_2\cdot CH_2\cdot CMe_2\end{matrix}$, and when hydrolysed is first converted into the amide of a hydroxy-acid, which then loses $2H_2O$, becoming the nitrile of nonenoic acid.

The view is expressed that in the conversion of pulenoneoxime into nonenonitrile the phases, *iso*oxime and amide of hydroxy-acid, are formed intermediately. This supposition accounts for the differences observed in the behaviour of cyclic ketone oximes; thus the oxime of menthone yields most readily an amide, since in this case the *iso*oxime, first formed, gives a hydroxy-acid, which from the position of the hydroxyl group does not readily lose water. In the case of camphoroxime on the other hand, the nitrile is produced even under the influence of dilute acids. K. J. P. O.

Essential Oil of Petit Grain. Paul Jeancard and C. Satie (*Bull. Soc. Chim.*, 1903, [iii], 29, 1088—1093. Compare Abstr., 1900, i, 511, and 1902, i, 45).—The authors have examined specimens of petit grain oil, distilled at intervals of a week during the month of June, in each of the years 1901, 1902, and 1903. The specific gravities, rotatory powers, solubilities in 70 per cent. alcohol, viscosities, acid, and saponification numbers, and percentage of alcohols of these oils are tabulated in the original. These tables indicate that both the rotatory power and viscosity of the oils are lower in colder seasons. By comparison of specimens of oil distilled in January (when only 1·4 per cent. of oil is

obtained) and in June, respectively, it was ascertained that the specific gravity, lævo-rotation, viscosity, and saponification numbers decrease during the first six months of the year and during the same period the oil becomes more soluble in 70 per cent. alcohol and the content of free alcohols increases. During the second half of the year, these changes are reversed, the alcohols being replaced by esters, whence it appears that a rising temperature increases both the yield of oil and the amount of free alcohols contained in it, whilst a falling temperature leads to the replacement of the alcohols by their esters. In orange flowers (yielding neroli oil), the formation of esters appears to be independent of the formation of alcohols, whilst in the branches (yielding petit grain oil) the total alcohol (uncombined and in the form of esters) is the same both in January and June. T. A. H.

The Alban of Gutta-percha. Alexander Tschirch (*Arch. Pharm.*, 1903, **241**, 481—495).—A specimen of gutta-percha at least 20 years old, which had become brittle, was extracted thoroughly with boiling 96 per cent. alcohol. The alban, which separated from the alcoholic extracts on cooling, was separated by fractional crystallisation into *spherite alban*, $C_{30}H_{44}O_2$, which melts at 152°, crystallises in spherites, and dissolves in hot alcohol, although not in cold, and *crystal-alban*, $C_{60}H_{80}O_3$, which melts at 227·5—228°, crystallises in plates, and dissolves with difficulty even in boiling alcohol. The residual gutta-percha was dissolved in chloroform, the solution filtered, 3/4 of the chloroform distilled off, and the residual solution poured into alcohol; the liquid was filtered from the sticky gutta which separated, and the filtrate allowed to remain, when flocculent aggregates separated, consisting of tiny needles of albanan (see later). In 100 parts of the substance were contained approximately: crystal-alban, 15; spherite-alban, 30; albanan, 0·1.

From a fresh sample of commercial gutta-percha, spherite-alban was obtained, but no crystal-alban; in place of the latter, an isomeride of the former, iso*spherite-alban*, $C_{30}H_{44}O_2$, was obtained; it melts at 142°, crystallises in needles or in spherites built up of needles, and dissolves in alcohol at 60°. A larger quantity of *albanan*, $C_{30}H_{44}O$, was obtained than from the old specimen; it melted at 61°, and was entirely insoluble in alcohol. In 100 parts of the sample were contained approximately: spherite-alban, 30; *iso*spherite-alban, 8; albanan, 1.

Several colour reactions of these substances are described.

Structural formulæ are suggested for them, the substances being represented as oxypolyterpenes. C. F. B.

Resin-Balsam of Pinus Laricio Poiret (Austrian Turpentine). Alexander Tschirch and Georg Schmidt (*Arch. Pharm.*, 1903, **241**, 570—588).—From a solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracts slowly (500 shakings were necessary for complete extraction) amorphous monobasic *laricopinic acid*, $C_{21}H_{30}O_3$, melting at 75—80°, and with acid number 177 and saponification

number about 230. One per cent. aqueous sodium carbonate then extracts crystalline monobasic *laricopinonic acid*, $C_{20}H_{28}O_4$, melting at 97°, and with acid number 183 and saponification number about 230; the anhydrous *silver*, *lead*, and *barium* salts were analysed; the acid could not be made to yield an acetyl derivative. From the remaining ethereal solution of the resin, 1 per cent. aqueous potassium hydroxide extracted nothing further. After complete extraction with potassium hydroxide, the ether was evaporated and the residue distilled with steam; an *essential oil* passed over slowly (5 months' distilling was necessary for complete separation), which for the most part boiled at 155—160° and had a sp. gr. 0·872; there remained behind a *resen* which could not be purified satisfactorily.

The resin itself had acid number 115 and saponification number about 120; it contained no *p*-coumaric acid, nor could a methoxyl group be detected in it. Water extracts a *bitter substance*. In the product of the dry distillation of the resin, formic, acetic, and succinic acids were detected; in the distillation of the mixed resin-acids, retene was obtained. Both the resin-acids were optically inactive. In 100 parts of the resin were contained: laricopinic acid, 25; laricopinonic acid, 34; essential oil, 35; resen, 2; water, bitter substance, and impurities, 3—4 parts.

A list is given below of the acids isolated up to the present by Tschirch and his collaborators from the resins of coniferous plants; those of one group were separated by extracting the ethereal solution of the resin with 1 per cent. aqueous ammonium carbonate, those of the other by subsequent extraction with 1 per cent. sodium carbonate. It is noteworthy that nearly all of them contain 2 atoms of oxygen in the molecule, and so must be either monocarboxylic or dihydroxy-compounds; in their power of forming salts, they behave as monobasic acids. Those not marked with an asterisk in the list exhibit a "saponification number" distinct from the acid number; it has been pointed out, however, that this is due, not to the hydrolysis of an ester, but to the slow fixation of more potash. Abietic acid may be taken as the type of the acids of this class; for the most part, they are derived from the genus *Abies*, and crystallise in plates. The acids marked with an asterisk have no "saponification number," or, rather, they have one practically identical with the acid number; of this class, pimaric acid may be taken as the type. These acids are derived for the most part from the genera *Picea* and *Dammara*, and are either amorphous or crystallise in rather shapeless aggregates. As a rule, any one resin contains only acids belonging to one of these two classes.

Acid.	Melting point.	Percentage of C.	Percentage of H.	Formula.	Acid number (direct).	Saponification number (hot).
Isolated by means of ammonium carbonate.						
Picipimarinic	130—135°	73·5	10·2	$C_{12}H_{20}O_2$	287	288
*Mancopalic	175	68·4	8·4	$C_8H_{12}O_2$	398	398
*Mancopalenic	100—105	67·8	9·7	$C_8H_{14}O_2$	392	392
Palabienic	110	75·3	9·3	$C_{13}H_{20}C_2$	188	235
*Kauric	192	72·0	9·2	$C_{10}H_{16}O_2$	330	335
*Canadic	135—136	77·3	11·9	$C_{19}H_{34}O_2$	192	192
*Piceapimarinic	130—132	75·1	9·4	$C_{13}H_{20}O_2$	262	262
*Pimarinic	118—119	75·8	10·0	$C_{14}H_{22}O_2$	252	255
Abienic	114—115	74·9	9·2	$C_{13}H_{20}O_2$	176	258
Laricopinic	75—80	76·4	9·1	$C_{21}H_{30}O_3$	177	243
α-Abietic	155	78·9	9·6	$C_{19}H_{28}O_2$	176	246
β-Abietic	158	79·0	9·5	$C_{19}H_{28}O_2$	174	189
Beljiabienic	113—115	75·0	9·3	$C_{13}H_{20}O_2$	182	255
Isolated by means of sodium carbonate.						
*α-Mancopalolic	85—90°	70·4	10·6	$C_{10}H_{18}O_2$	326	330
*β-Mancopalolic	83—88	70·4	10·5	$C_{10}H_{18}O_2$	323	330
α-Palabietinolic	90—95	77·4	9·6	$C_{16}H_{24}O_2$	194	312
β-Palabietinolic	90—95	77·2	9·5	$C_{16}H_{24}O_2$	190	299
*α-Kaurolic	81—83	73·4	10·1	$C_{12}H_{20}O_2$	279	282
*β-Kaurolic	85—87	73·3	10·1	$C_{12}H_{20}O_2$	278	283
*Silveolic	138	76·2	9·3	$C_{14}H_{20}O_2$	224	228
Canadolic	143—145	79·2	9·7	$C_{19}H_{28}O_2$	192	328
Laricinolic	147—148	79·4	9·7	$C_{20}H_{30}O_2$	190	396
Abietolic	145—153	79·9	9·6	$C_{20}H_{28}O_2$	189	350
Laricopinonic	97	72·3	8·4	$C_{20}H_{28}O_4$	181	257
*γ-Abietic	153—154	79·1	9·8	$C_{19}H_{28}O_2$	182	183
*Pimaric	144—146	79·4	9·9	$C_{20}H_{30}O_2$	186	186
*Piceapimaric	144—145	79·5	9·9	$C_{20}H_{30}O_2$	192	191
Palabietic	153—154	79·1	9·9	†$C_{19}H_{28}O_2$	182	321
α-Abietinolic	95—96	77·3	9·5	$C_{16}H_{24}O_2$	218	286
β-Abietinolic	93—94	77·2	9·4	$C_{16}H_{24}O_2$	217	266
α-Larinolic	80—81	78·9	9·7	$C_{18}H_{26}O_2$	199	316
β-Larinolic	85—86	78·7	9·7	$C_{18}H_{26}O_2$	196	302
*α-Canadinolic	95	78·6	10·6	$C_{19}H_{30}O_2$	200	201
*β-Canadinolic	95	78·6	10·6	$C_{19}H_{30}O_2$	198	199
*α-Piceapimarolic	95	79·8	11·6	$C_{25}H_{44}O_2$	166	166
*β-Piceapimarolic	94	79·6	11·7	$C_{25}H_{44}O_2$	165	165
*α-Pimarolic	90—91	78·7	9·6	$C_{18}H_{26}O_2$	196	195
*β-Pimarolic	89—96	78·8	9·6	$C_{18}H_{26}O_2$	196	199
*α-Silvinolic	below 100	75·8	11·0	$C_{15}H_{26}O_2$	230	233
*β-Silvinolic	below 100	75·0	10·9	$C_{14}H_{24}O_2$	244	251
*α-Picipimarolic	95—96	78·2	10·4	$C_{18}H_{28}O_2$	200	200
*β-Picipimarolic	93—94	78·6	10·3	$C_{18}H_{28}O_2$	206	207
Beljiabietic	153—154	79·3	9·8	†$C_{19}H_{28}O_2$	182	333
α-Beljiabietinolic	95—96	77·7	9·8	$C_{16}H_{24}O_2$	210	274
β-Beljiabietinolic	95—96	77·7	9·8	$C_{16}H_{24}O_2$	210	257

* Has no "saponification number." † Or $C_{20}H_{30}O_2$.

C. F. B.

American Colophony. By Alexander Tschirch and B. Studer (*Arch. Pharm.*, 1903, **241**, 495—522).—A solution of the resin in ether was shaken repeatedly with 1 per cent. aqueous ammonium carbonate; after 300—400 repetitions, a constant amount of acid, equal to 0·025 per cent. of the resin, was dissolved each time, and as about the same amount continued to be dissolved up to the 600th repetition, the process was then discontinued Attempts to obtain the crystalline acid by using a mixture of methyl and ethyl alcohols or light petroleum as a solvent were unsuccessful. At last, it was found possible, by treating an alcoholic solution of the acid with alcoholic lead acetate, to effect a separation into a lead salt insoluble in alcohol and an acid which remained in solution without forming a lead salt at all. The corresponding acids can then be crystallised separately from alcohol; they appear to be isomeric and to have the molecular formula $C_{19}H_{28}O_2$. The first, *a-abietic acid*, softens at 143° and is completely melted at 155°, and is a monobasic acid, with acid number 177 and saponification number 247. The second, *β-abietic acid*, softens at 145° and is completely melted at 158°, and is a monobasic acid, with acid number 174 and saponification number 190.

From the ethereal solution of the resin, 1 per cent. aqueous sodium carbonate now extracted another acid, *γ-abietic acid*, isomeric with the first two; the extraction was complete after 20 operations. This acid melts at 153—154°, but probably at 161° when pure; it has $[a]_D - 37·75°$ and is monobasic, with acid number 183 and saponification number 186; when heated with hydriodic acid, it does not evolve methyl iodide, and it is not changed when boiled with acetic anhydride; it was distilled to a large extent unchanged in an iron apparatus under diminished pressure. The behaviour of each of these three acids towards the usual cholesterol reagents is described; a *silver* salt of each was prepared and analysed.

From the residual ethereal solution, neither 1 nor 10 per cent. aqueous sodium hydroxide extracted any further acid. The ether was evaporated, and the residue distilled with steam; the distillation had to be continued for $1\frac{1}{2}$ months to drive over all the *essential oil*, although but little of this was present. The *resen* remaining could only be obtained as a brown mass that softened in the hand, and therefore was not analysed.

From 100 parts of the resin were obtained, approximately (the loss in manipulation being about 10 per cent.): abietic acids, *a* 30, *β* 22, *γ* 32; essential oil, 0·4—0·7; resen, 5—6; impurities, 0·1. A small quantity of an amorphous *bitter substance* could be extracted with water.

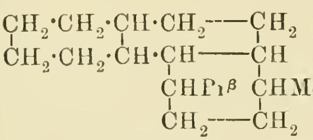
An examination was made of the abietic acid obtained by previous investigators, namely, that obtained by Maly, by washing the resin with 70 per cent. alcohol until white, and then crystallising it from strong alcohol; by Flückiger, by leading dry hydrogen chloride into an alcoholic solution of the resin; and by Tschirch, by extracting an ethereal solution of the resin with aqueous sodium hydroxide. The acid obtained by the first method was actually separated into the three isomeric acids described above.

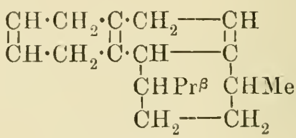
Fahrion (Abstr., 1902, i, 165) has shown that the part of colo-

phony less soluble in light petroleum has a higher ester number, and that this part increases in amount when the resin is exposed in the state of powder to light and air ; he attributes this to autoxidation. It may be merely molecular transformation, for the α-abietic acid, which has a high ester number, is less soluble in light petroleum than the two isomeric acids, which have no ester number, or a very low one.

A table is given of the acid and saponification numbers of 13 samples of American colophony ; in the case of some of the samples, the percentage insoluble in light petroleum is also indicated. C. F. B.

Constitution of Abietic Acids. ALEXANDER TSCHIRCH and B. STUDER (*Arch. Pharm.*, 1903, **241**, 523—545).—The reactions of the resin-acids of *Coniferæ* are discussed, and the various formulæ proposed for them are considered. The conclusion is drawn that Tschirch's view of them (*Pharm. Post*, 1900, No. 43 ; *J. de Pharm. et de Chim.*, Nov. 1900), as derived from fichtelite or from a hydrogenised retene, octohydroretene, has most in its favour ; "it is in harmony with all the observed facts and is contradicted by none of them."


Fichtelite.


Octohydroretene.

On account of the undoubted relation of the resin-acids to the cholesterols, phytosterols are more likely than tannins to be the parent substances of these acids. But no impassable gulf is fixed between the two classes of compounds ; some of the resinotannols, substances resembling tannins, in some reactions yield derivatives of benzene ; in others, derivatives of terpenes, and, consequently, they may be regarded as containing a combination of a benzene with a terpene ring.

C. F. B.

Rhein from Aloe-emodin. OTTO A. OESTERLE (*Arch. Pharm.*, 1903, **241**, 604—607).—Aloe-emodin was oxidised with chromic acid in boiling acetic acid solution, the liquid poured into water, and the precipitate dried and extracted with chloroform in a Soxhlet apparatus. The residue was found to be identical with the rhein of rhubarb (Hesse, Abstr., 1900, i, 41 ; Tschirch and Heuberger, Abstr., 1903, i, 108). Much of the emodin escaped oxidation. C. F. B.

Solanin. SIMON ZEISEL and J. WITTMANN (*Ber.*, 1903, **36**, 3554—3558).—A criticism of Hilger and Merkens (Abstr., 1903, i, 846). The formation of crotonaldehyde on decomposing solanin by dilute sulphuric acid is doubted ; the only aldehyde formed is methylfurfuraldehyde in small quantity. The sugar obtained from solanin does not consist exclusively of dextrose, but contains a large proportion

of rhamnose as well as another carbohydrate, which is not easily isolated. Crystalline dextrose cannot be obtained from the mixture of sugars. W. A. D.

Ceroptene. Walter C. Blasdale (*J. Amer. Chem. Soc.*, 1903, 25, 1141—1152).—The fronds from *Gymnogramme triangularis*, the "golden-back" fern of the Pacific coast, were extracted with benzene or light petroleum and, from the extract, crystals of ceroptene separated. The mother liquor, from which the ceroptene had been removed, contained cerotic acid. *Ceroptene*, $C_{18}H_{18}O_4$, forms tabular or prismatic triclinic crystals [$a:b:c = 8\cdot5353:1:1\cdot0138$; $\alpha = 112°13'$, $\beta = 92°12'$, $\gamma = 94°33'$] of a sulphur-yellow colour, melts at 135°, and has a sp. gr. 1·1976 at 15°/15°. It is readily dissolved by dilute solutions of alkali hydroxides; its *potassium*, *barium*, *silver*, and *lead* salts are described. The *iodo*-derivative, prepared by the action of hydriodic acid on a solution of ceroptene in glacial acetic acid at 60°, separates in needles and melts at 182°. A. McK.

Brazilin and Hæmatoxylin. Josef Herzig and Jacques Pollak (*Ber.*, 1903, 36, 3713—3715. Compare Abstr., 1902, i, 482; 1903, i, 270, 508, 713).—Acetyltetramethylhæmatoxylin on oxidation yields tetramethylhæmatoxylone, which reacts with hydroxylamine hydrochloride, forming a compound having the composition of an *oxime*, $C_{20}H_{20}O_6\colon N\cdot OH$. The *acetyl* derivative melts and decomposes at 179—183°. The methods adopted by the authors for the preparation of isomeric dehydro-derivatives from trimethylbrazilone (*loc. cit.*, 508) have also been applied in this case. Direct acetylation yields *α-acetyltetramethyldehydrohæmatoxylin*, melting at 194°, the action of sulphuric acid produces the β-compound, melting at 194—195°, a mixture of the two melting at 168—182°, a γ-compound could not be prepared. *α-Pentamethyldehydrohæmatoxylin*, prepared by the action of diazomethane on the α-tetramethyl derivative, melts at 168—170°, the β-compound at 175—176°, a mixture of the two at 145—155°. The two β-compounds are identical with those obtained by Kostanecki and Rost (this vol., i, 646), and described as derivatives of 5-(or 10-)-hydroxy-1:2:7:8-tetramethoxybrazan, the melting points differ slightly from those given by these authors. C. H. D.

Theory of Dyeing. Georg von Georgievics (*Ber.*, 1903, 36, 3787—3790).—A criticism of Binz and Schröter's paper on the same subject (Abstr., 1903, i, 109; see also 1902, i, 635). E. F. A.

Sulphur Dyes from the Phenols and their Derivatives. Chemische Fabrik Grünau; Landshoff & Meyer, Aktien-Gesellschaft (D.R.-P. 144104).—Compounds such as phenols, nitro- and amino-phenols, and diphenylamine derivatives, which yield dyes on fusion with alkali sulphide and sulphur, also form dyes when mixed with sodium hydroxide and sodium thiosulphate and heated at 200—280°. C. H. D.

Derivatives and Oxidation Products of Nitropyromucic Acid. R. Marquis (*Compt. rend.*, 1903, **137**, 520—521).—*Methyl nitropyromucate*, prepared by the method already described for the ethyl ester (Abstr., 1903, i, 49), crystallises in nacreous lamellæ, melts at 78·5°, and is more soluble in alcohol than the ethyl ester.

Nitropyromucyl chloride, obtained by the action of phosphorus pentachloride on nitropyromucic acid dissolved in chloroform, crystallises in greasy lamellæ, melts at 38°, is soluble in chloroform and ether, and is slowly decomposed by cold water. The *amide* forms white, silky crystals and melts at 161°. The *anilide* crystallises in citron-yellow needles and melts at 180°. The p-*toluidide* forms yellow prisms and melts at 162°.

When oxidised by sodium peroxide, ethyl nitropyromucate furnishes fumaric acid, indicating that the nitro-group occupies either the 3- or 4-position (compare Abstr., 1903, i, 49, and Hill and White, Abstr., 1902, i, 388). T. A. H.

Esters of *iso*Pyromucic Acid. G. Chavanne (*Compt. rend*, 1903, **137**, 992—993).—*iso*Pyromucic acid is not readily esterifiable (Abstr., 1901, i, 649), but the sodium salt, prepared by the action of sodium methoxide on the acid in methyl alcoholic solution, reacts on warming gently with ethyl or methyl sulphate. The ester formed is purified by crystallisation from dry ether. *Methyl* iso*pyromucate*, $C_5H_3O_3Me$, forms long, colourless needles melting at 60° and boiling at 130—135° under 20 mm. pressure. *Ethyl* iso*pyromucate* melts at 52°, and may also be distilled under reduced pressure. *Benzyl* iso*pyromucate* forms highly refractive prisms melting at 71°, and may be prepared in small yield by the direct action of benzyl chloride on sodium *iso*pyromucate. The methyl and ethyl esters are very soluble in water or alcohol, less so in ether, the benzyl ester is insoluble in water, but dissolves readily in organic solvents. They become yellow on exposure to light, and are very stable towards acids, resembling phenyl ethers rather than esters. C. H. D.

Quinonoid Derivatives of Benzopyranol from 3 : 5-Dimethoxybenzoylacetophenone. II. Carl Bülow and Gustav Riess (*Ber.*, 1903, **36**, 3607—3610. Compare Abstr., 1903, i, 101, 647, 715).—3 : 5-Dimethoxybenzoylacetophenone condenses with pyrogallol in glacial acetic acid in presence of hydrogen chloride, forming 4 : 7-*anhydro*-7 : 8-*dihydroxy*-2-*phenyl*-4-*di*-m-*methoxyphenyl*-1 : 4-*benzopyranol hydrochloride*, $C_{23}H_{18}O_5,HCl,H_2O$, which crystallises from acidified alcohol in reddish-brown needles. The *base*, obtained by the treatment of an alcoholic solution of the hydrochloride with sodium acetate, crystallises in bluish-black needles melting at 225—230°, and dissolving in benzene or chloroform to a blue solution, insoluble in water or dilute sodium hydroxide. The *picrate* forms groups of small needles melting and decomposing at 215—218°.

Phloroglucinol yields a similar derivative, 5 : 7-*dihydroxy*-2-*phenyl*-4-*di*-m-*methoxyphenyl*-1 : 4-*benzopyranol*, crystallising in brownish-red needles melting at 215—220°. The *hydrochloride* forms brick-red needles decomposing at 205°. Picric acid precipitates the *picrate* of

the anhydrobenzopyranol from alcoholic solution in vermilion crystals melting and decomposing at 205°. C. H. D.

Condensation Products of Tetramethyldiaminophenyloxanthranol with Benzene, Toluene, and Dimethylaniline. Albin Haller and Alfred Guyot (*Compt. rend.*, 1903, **137**, 606—611. Compare Abstr., 1901, i, 350; 1903, i, 200, 348).—When a mixture of equal parts of benzene and tetramethyldiaminophenyloxanthranol (Abstr., 1899, i, 350) is treated with five times its weight of sulphuric acid, there is formed an *additive product*, $C_{30}H_{30}O_2N_2$. This separates from benzene solution on adding light petroleum in colourless crystals, melts at 140°, is soluble in benzene and chloroform, and slightly so in alcohol and ether. Its *salts* are crystalline, and dissolve in water to form intensely orange-coloured solutions; the *zinc chloride* derivative forms red crystals. With hydroxylamine, a *condensation product*, $C_{30}H_{29}ON_3$, is obtained, which crystallises in slender needles and melts at 210°. The corresponding *substance*, $C_{36}H_{34}N_4$, produced by condensation with phenylhydrazine, forms colourless crystals and melts at 200°.

Similarly, when toluene is condensed with tetramethyldiaminophenyloxanthranol, a *product*, $C_{31}H_{32}O_2N_2$, is obtained, which forms colourless crystals, melts at 163—164°, and has solubilities similar to those of its lower homologue. The *salts* are crystalline, and give intense orange-red aqueous solutions. The derivative, obtained by condensation with hydroxylamine, forms slender, colourless needles and melts at 245°, and that with phenylhydrazine, pale yellow crystals melting at 220°.

To these additive products and their hydroxylamine and phenylhydrazine derivatives respectively, the authors assign formulæ of the following type:

$$C_6H_4<\begin{matrix}CR(OH)\\CR(OH)\end{matrix}>C_6H_3\cdot NMe_2 \qquad OH\cdot N\langle C_6H_4\langle\begin{matrix}C\cdot R\\C\cdot R\end{matrix}\rangle C_6H_3\cdot NMe_2$$

$$NHPh\cdot N\langle C_6H_4\langle\begin{matrix}CR\\CR\end{matrix}\rangle C_6H_3\cdot NMe_2 .$$

in which R may be either phenyl or tolyl. Similar formulæ have already been assigned by the authors to phthalyl-green, produced by condensing dimethylaniline with tetramethyldiaminophenyloxanthranol and its corresponding derivatives (Abstr., 1903, i, 200). T. A. H.

The Union of Dinaphthaxanthonium Salts with Phenols. Robert Fosse (*Compt. rend.*, 1903, **137**, 858—860).—Dinaphthaxanthonium salts, $CH\langle\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\rangle OX$, interact with sodium compounds of phenols to give derivatives of *p*-hydroxyphenyldinaphthaxanthen, $OH\cdot C_6H_4\cdot CH<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O$; the same compounds can also be obtained by the condensation of one molecule of a hydroxybenzaldehyde with two molecules of β-naphthol. Thus *p*-hydroxyphenylnaphthaxanthen is

formed (*a*) from dinaphthaxanthonium chloride and sodium phenoxide, (*b*) from *p*-hydroxybenzaldehyde and β-naphthol, the product melts at 207° and crystallises with one molecule of alcohol. Analogous methods led to the formation of 4-hydroxy-3-methoxyphenylnaphthaxanthen melting at 210°, and of 2-hydroxynaphthylnaphthaxanthen, which melts at 273°. S. S.

Decacyclene [Trinaphthylenbenzene] and Dinaphthylenthiophen. II. KARL DZIEWOŃSKI (*Ber.*, 1903, **36**, 3768—3774. Compare Abstr., 1903, i, 431).—[With PAUL BACHMANN.]—*a-Bromodinaphthylenthiophen*, $C_{10}H_6<\overset{C—C}{\underset{C\cdot S\cdot C}{||\quad ||}}>C_{10}H_5Br$, prepared by the action of bromine on dinaphthylenthiophen, crystallises from chloroform in small, bulky, red needles and melts at 202°. The *aa-dibromo*-derivative, $C_{24}H_{10}SBr_2$, crystallises from nitrobenzene in glistening, red needles and melts at 362—363°. Both compounds yield α-bromonaphthalic anhydride, $C_{10}H_5Br<\begin{matrix}CO\\CO\end{matrix}>O$, when oxidised with chromic acid.

[With ELIGIO DOTTA.]—*aa-Dinitrodinaphthylenthiophen*,

$$NO_2\cdot C_{10}H_6<\overset{C—C}{\underset{C\cdot S\cdot C}{||\quad ||}}>C_{10}H_6\cdot NO_2,$$

crystallises from nitrobenzene in small, grey-violet needles, and, when heated, sublimes and partially decomposes; it yields α-nitronaphthalic anhydride, $NO_2\cdot C_{10}H_5<\begin{matrix}CO\\CO\end{matrix}>O$, when oxidised.

Trinitrodecacyclene, $C_{36}H_{15}(NO_2)_3$, forms red, glistening needles, is almost insoluble in all solvents but quinoline, and, when heated, explodes (puffs) without melting or subliming.

Tribromodecacyclene, $C_{36}H_{15}Br_3$, crystallises from nitrobenzene in minute, yellow needles, softens at 380°, and melts at 397—400°.

Nonochlorodecacyclene, $C_{36}H_9Cl_6$, is a yellow powder, much more soluble than the preceding compounds, and melts at 215—218°. T. M. L.

Alkaloids of Angostura Bark. HEINRICH BECKURTS and GUSTAV FRERICHS (*Chem. Centr.*, 1903, ii, 1010—1011; from *Apoth. Zeit.*, 18, 697—699. Compare Abstr., 1892, 642).—The crystalline alkaloids of angostura bark, cusparine, galipine, galipidine, and cusparidine are stronger bases than the amorphous alkaloids of the bark, and may be separated from the ethereal extract by means of their tartrates or acetates. Galipidine is a tertiary base and forms a methyl derivative. The yellow colour of its salts is due to the presence of a small quantity of galipine, which disappears when the alkaloid is submitted to the action of nascent hydrogen; the base then melts at 113°. Cusparine, $C_{20}H_{19}O_3N$, is also a tertiary base containing a methoxyl group, but no hydroxyl groups; it forms a methyl derivative. When fused with potassium hydroxide, it does not decompose directly into a base and an aromatic acid (compare Körner and Boehringer, Abstr., 1884, 341), but by the action of the heat alone is converted into the base pyrocusparine, melting at 350°, which is then attacked by the

alkali and yields protocatechuic acid. When cusparine is heated with carbimide for a short time only, pyrocusparine is formed together with a *base* which melts at 142°. Galipidine also yields protocatechuic acid, and, like cusparine, is not readily hydrolysed. *Nitrocusparine*, prepared by the action of dilute nitric acid on cusparine, crystallises in yellow needles.

After separating the crystalline alkaloids from the ethereal extract by shaking with dilute hydrochloric acid or from a solution in light petroleum by means of picric acid, another alkaloid, cuspareine, may be isolated from the liquid bases which are left. One hundred kilograms of bark yield 7 grams of this alkaloid. *Cuspareine*, $C_{34}H_{36}O_2N_5$(?), is soluble in light petroleum, crystallises in needles, melts at 54°, and boils with slight decomposition at about 300°. It does not form salts, but gives a deep red coloration with oxidising agents, and combines with methyl iodide. The liquid bases from which cuspareine has been extracted distil without decomposition at higher temperatures, but attempts to prepare crystalline salts failed.

When narceine is melted with carbimide (compare Abstr., 1903, i, 717), the ammonia liberated by the decomposition of the latter compound converts the former into narceineimide and an indifferent compound which melts at 192°. Berberine, under similar conditions, yields an alkaloid which forms yellow salts and serves as an excellent indicator for alkalis, ammonia, and carbonates, and also for the titration of alkaloids in presence of a layer of chloroform. Morphine, strychnine, and papaverine are not affected by melting with carbimide.

E. W. W.

Preparation of Caffeine-ethylenediamine. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 142896).—*Caffeine-ethylenediamine*, prepared by heating chloro- or bromo-caffeine with ethylenediamine in alcoholic solution, separates from alcohol in crystals melting at 184° and dissolves readily in water, hot chloroform, or alcohol. The *acetyl* derivative melts at 282° and the *lactyl* derivative at 240°. A small quantity of the sparingly soluble dicaffeine-ethylenediamine is formed at the same time.

C. H. D.

Chemistry of Chelidonine. JULIUS O. SCHLOTTERBECK and HAROLD C. WATKINS (*Pharm. Arch.*, 1903, 6, 141—144. Compare Abstr., 1902, ii, 100).—Chelidonine, $C_{20}H_{19}O_5N,H_2O$, melts at 136° and has $[\alpha]_D$ +115°24′. Its *acetyl* derivative, $C_{20}H_{18}O_4N\cdot OAc$, crystallises in white plates and melts at 161°; the corresponding *benzoyl* derivative melts at 217°. When the alkaloid is heated with zinc dust in an atmosphere of hydrogen, ammonia is produced together with small quantities of a substance which forms small, nodular crystals and has a phenanthrene-like odour. Attempts to oxidise the alkaloid resulted in breaking down the molecule completely with formation of carbon dioxide, ammonia, and probably methylamine, no intermediate product being obtained. Phenylhydrazine does not react with it.

E. G.

A New Isomeric Change of Cinchonicine. Zdenko H. Skraup and W. Egerer (*Monatsh.*, 1903, 24, 669—680. Compare Abstr., 1903, i, 649, 715).—When heated with concentrated sulphuric acid at 100° for 45 minutes, cinchonicine oxalate yields β-*iso*-ψ-cinchonicine, recognised by comparison of its hydriodide (m. p. 150°) and its hydrochloride with the salts of β-*iso*-ψ-cinchonicine obtained by Pasteur's reaction from β-*iso*cinchonine. When the heating with sulphuric acid is continued for 5 hours, the hydriodide obtained from the product sinters at 150° and melts at 213—214°.

Cinchonicine forms an additive *compound* with hydrogen iodide in the same manner as does cinchonine. The close relationships between cinchonine and β-*iso*cinchonine and between β-*iso*cinchonine and β-*iso*-ψ-cinchonicine have been previously shown. As β-*iso*-ψ-cinchonicine has now been formed from cinchonine through cinchonicine, it follows that the "second half" of the cinchonicine molecule must closely resemble that of the other cinchonine alkaloids. G. Y.

The Synthesis of Nicotine. Amé Pictet (*Compt. rend.*, 1903, 137, 860—862).—The author describes the synthesis of an inactive nicotine (Abstr., 1895, i, 627; 1898, i, 688; 1900, i, 685), which he finds to be identical with that produced by heating an aqueous solution of the sulphate of the natural product. By fractionally crystallising the tartrate of the synthetical base, it is possible to isolate a salt, $C_{10}H_{14}N_2,2C_4H_6O_6,2H_2O$, which melts at 88° and has $[\alpha]_D + 25\cdot1°$. The base obtained from this tartrate by treatment with sodium hydroxide boils at 246·1° under 735 mm. pressure, has a sp. gr. 1·008 at 22°/4°, and $[\alpha]_D - 161\cdot19°$ at 25·5°. Nicotine derived from natural sources boils at 246·1—246·2° under 730 mm. pressure, has a sp. gr. 1·009 at 20°/4°, and $[\alpha]_D - 161\cdot55°$ at 20°. The synthetical and natural products are therefore identical. S. S.

Methylbetaine of Papaveric Acid. Guido Goldschmiedt and Otto Hönigschmid (*Monatsh.*, 1903, 24, 681—705. Compare Schranzhofer, Abstr., 1894, i, 59; Goldschmiedt and Kirpal, Abstr., 1897, i, 131).—Schranzhofer's yellow substance, melting at 192—194°, is now found to be the methylbetaine of papaveric acid as stated by that author. Goldschmiedt and Kirpal were mislead by an error in the methoxyl determination (see Abstr., 1903, ii, 578).

The methylbetaine of papaveric acid is formed by the action of methyl iodide on papaveric acid in methyl alcoholic solution at 100°, on papaveric-β-methyl ester alone or in methyl alcoholic solution at 100°, on papaveric-γ-methyl ester in methyl alcoholic solution at 100°, and on papaveric acid in aqueous sodium carbonate solution.

Methyl iodide has no action at 100° on papaveric acid or its γ-methyl ester in absence of a solvent, on dimethyl papaverate, or on papaveric anhydride. The methylbetaine is formed by the action of dimethyl sulphate on papaveric acid in aqueous potassium hydroxide solution.

When papaveric-β-methyl ester is heated at its melting point, it yields the γ-methyl ester, which at its melting point decomposes with evolution of carbon dioxide. In neither case is the methylbetaine formed (compare Willstätter, Abstr., 1902, i, 266; Kirpal, Abstr., 1902, i, 564).

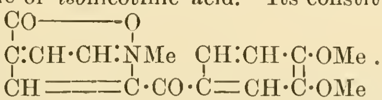
The methylbetaine of papaveric acid is not decomposed by boiling fuming hydrochloric acid; when boiled with aqueous barium hydroxide, it yields veratric and apophyllenic acids, and is therefore to be considered to be α-veratrylapophyllenic acid (compare Abstr., Kirpal, 1901, i, 564). A similar hydrolysis takes place with papaveraldine methiodide, which yields veratric acid when boiled with aqueous potassium hydroxide.

The *platinichloride* of the methylbetaine of papaveric acid has the constitution $(C_{17}H_{15}O_7N)_4,2HCl,H_2PtCl_6,8H_2O$, and the residue, after heating at 125°, $(C_{17}H_{15}O_7N)_4,H_2PtCl_6$. The *aurichloride*,

$$C_{17}H_{15}O_7N,HAuCl_4,H_2O,$$

crystallises in long, glistening, yellowish-red leaflets.

The *methylbetaine* of *pyropapaveric acid*, $C_{16}H_{17}O_5N,3H_2O$, is formed by successive action of methyl iodide and silver oxide on pyropapaveric acid and by heating the methylbetaine of papaveric acid with phenol. It crystallises in white needles, melts at 182°, and is soluble in water or alcohol. The *platinichloride*, $(C_{16}H_{15}O_5N)_2,H_2PtCl_6,2H_2O$, crystallises in glistening, yellow needles and loses $2H_2O$ at 110°. When boiled with aqueous barium hydroxide or potassium hydroxide, the methylbetaine of pyropapaveric acid yields veratric acid and the methylbetaine of *iso*nicotinic acid. Its constitution is represented by the formula



G. Y.

Pyrrolidine-3-carboxylic Acid. Hermann Pauly and Alex. Hültenschmidt (*Ber.*, 1903, 36, 3351—3370, 3687. Compare Wallach, Abstr., 1902, i, 79).—2 : 2 : 5 : 5-*Tetramethylpyrrolidine-3-carboxylic acid*, prepared by the action of hydrochloric acid on tetramethylpyrrolidinecarboxylamide (obtained by the action of ammonia on the dibromide of triacetoneamine), crystallises with H_2O in prismatic needles, is easily soluble in water, and melts and decomposes at 220°. The *hydrochloride* forms anhydrous needles easily soluble in water and decomposes at 234°; the *platinichloride*, $(C_9H_{17}O_2N)_2,H_2PtCl_6$, decomposes at 216°; the *methyl ester* is a colourless liquid, boils at 206° (corr.), and has a sp. gr. 0·958 at 24°; the *ethyl ester* boils at 217° (corr.).

1 : 2 : 2 : 5 : 5-*Pentamethylpyrrolidine-3-carboxylic acid*, crystallises with $2\frac{1}{2}H_2O$ in plates melting at 129°, and is very easily soluble in water, less so in alcohol; the *hydrochloride* crystallises in prisms and melts and decomposes at 256°; the *platinichloride* forms orange crystals melting and decomposing at 197—198°; the *methyl ester* boils at 218° (corr.), and its hydriodide melts at 192°; the ethyl ester boils at 227° (corr.) and has a sp. gr. 0·955 at 15°. The two acids, in contradistinction to the pyrrolidine-2-carboxylic acids (Fischer, Abstr., 1902, i, 699), are almost tasteless; physiologically, the pentamethyl acid is the more powerful poison.

Pentamethylpyrrolidinecarboxylamide forms a *methiodide*, crystallising in flat, prismatic needles and decomposing at 255°; when heated with potassium hydroxide, this is converted into γ-*dimethylamino*-α-iso*propylidene*iso*hexoamide*, $NMe_2\cdot CMe_2\cdot CH_2\cdot C(:CMe_2)\cdot CO\cdot NH_2$, which

melts at 98°, boils at 170° under 13 mm. pressure, and crystallises from ether; it yields a sparingly soluble *dibromide* and a *methiodide*, forming prismatic crystals melting at 184°. The latter, when digested with silver oxide and subsequently heated, loses trimethylamine, forming *di*iso*propylidenepropionamide*, $CMe_2:CH\cdot C(CO\cdot NH_2):CMe_2$, which boils at 142—145° under 14 mm. pressure, solidifies to a wax-like substance melting at 59°, and unites with at least two molecules of bromine; the amide is very resistant towards hydrolytic agents.

On heating tetramethylpyrrolidine-3-carboxylic acid at 220°, it is decomposed, a portion distilling over at this temperature, whilst a solid residue remains in the flask. The distillate is *ε-amino-βε-dimethyl-Δ^β-hexene*, $NH_2\cdot CMe_2\cdot CH_2\cdot CH:CMe_2$, which boils at 150°, and forms a *platinichloride*, crystallising in orange-red prisms melting at 172°. When oxidised with permanganate, it yields acetone and β-amino*iso*valeric acid. In ethereal solution, it unites with hydrogen chloride to form a sparingly soluble *dihydrochloride*, which may have one of the formulæ $CMe_2Cl\cdot CH_2\cdot CH_2\cdot CMe_2\cdot NH_2,HCl$ or

$$CHMe_2\cdot CHCl\cdot CH_2\cdot CMe_2\cdot NH_2,HCl.$$

With bromine, it forms a *dibromide*, and this yields a *hydrobromide*. The solid residue is *2-dimethyl-*4-iso*propylidene-5-pyrrolidone*, $NH<\begin{matrix}CMe_2\cdot CH_2\\ CO\text{——}C:CMe_2\end{matrix}$, which crystallises from ether in quadrilateral plates melting at 121°, and forms a *dibromide* melting at 148°.

When heated, pentamethylpyrrolidine-3-carboxylic acid decomposes into *ε-methylamino-βε-dimethyl-Δ^β-hexene*, boiling at 167—168° and forming an orange-yellow *platinichloride* melting at 160°, and *1 : 2 : 2-trimethyl-*4-iso*propylidene-5-pyrrolidone*, which boils at 127—128° under 15 mm. pressure. E. F. A.

Tetramethylpyrroline-3-carboxylic Acid. Hermann Pauly and Alex. Hültenschmidt (*Ber.*, 1903, 36, 3371—3372).—When tetramethylpyrroline-3-carboxylic acid is heated at 290—310°, disruption of the ring does not take place, but carbon dioxide is eliminated with the formation of tetramethylpyrroline, $\begin{matrix}CH\cdot CMe_2\\ \Vert\\ CH\cdot CMe_2\end{matrix}>NH$. E. F. A.

Phthalones. Robert Gaebelé (*Ber.*, 1903, 36, 3913—3923).—Both pyrophthalone and *iso*pyrophthalone (von Hüber, Abstr., 1903, i, 576) are dissolved by dilute alkali hydroxides, and, on precipitating the salt of the hydroxy-acid obtained in each case with acid, the same substance, namely, the unsymmetrical phthalone, $CO<\begin{matrix}C_6H_4\\ O\end{matrix}>C:CH\cdot C_5NH_4$, is obtained. The author hence considers that the two forms

$$\text{I. } C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>CHR \quad \text{and II. } CO<\begin{matrix}C_6H_4\\ O\end{matrix}>C:CHR$$

are pseudomeric, and that under the influence of alkali the symmetrical form I undergoes transformation into the form II, which then undergoes fission, forming a hydroxy-acid. This view is supported by the fact that both of the pyrophthalones, on reduction by zinc dust in alkaline solution, give the same *dihydrostilbazole*-o-*carboxylic acid*,

$C_5NH_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$, the *hydrochloride* of which crystallises from dilute hydrochloric acid and melts at 158°; on attempting to liberate the acid from the hydrochloride by means of sodium carbonate, an *anhydride*, probably *pyridyl-a-hydrindone*,

$$C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CH{\cdot}C_5NH_4,$$

is obtained, which crystallises from alcohol in orange-red needles and melts at 207·5—208°.

8-*Methylquinophthalone*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CH{\cdot}C_{10}H_8N$, prepared by heating 8-methylquinaldine with phthalic anhydride and zinc chloride for 3—4 hours at 180—190°, crystallises from glacial acetic acid or chloroform in yellow needles, melts at 276·5—277°, and can be obtained only in one form. With an excess of bromine in chloroform solution, it combines to form a red, crystalline *perbromide*,

$$C_6H_4{:}(CO)_2{:}CBr{\cdot}C_{10}H_8N,HBr,Br_2,$$

which is decomposed by alcohol giving the *monobromo*-derivative, $C_6H_4{:}(CO)_2{:}CBr{\cdot}C_{10}H_8N$. This substance melts at about 170°, but subsequently solidifies to a yellow mass, which melts at 213—215°; it is suggested that isomeric change to the unsymmetrical form

$$CO<\begin{matrix}C_6H_4\\O\end{matrix}>C{:}CBr{\cdot}C_{10}H_8N$$

here occurs.

N-*Methyl*-8-*methylquinophthaline*, $C_6H_4<\begin{matrix}CO\\C(NMe)\end{matrix}>CH{\cdot}C_{10}H_8N$, prepared by heating 8-methylquinophthalone with alcoholic methylamine for 6—7 hours at 200°, crystallises from chloroform on adding methyl alcohol in red needles and melts at 205°. N-*Ethyl*-8-*methylquinophthaline* forms orange-red needles melting at 198°, and N-n-*butyl*-8-*methylquinophthaline*, red needles melting at 178°; N-*benzyl*-8-*methylquinophthaline* melts at 208°.

6-*Phenylpyrophthalone*, $C_{20}H_{13}O_2N$, prepared by condensing 2-methyl-6-phenylpyridine with phthalic anhydride, crystallises from acetic acid or chloroform in golden needles, melts at 263°, and yields, with bromine, an unstable *perbromide*, $C_{20}H_{13}O_2NBr_4$, which, by alcohol, is converted into a yellowish-white *monobromo*-derivative melting at 131°. On reduction with zinc dust and acetic acid, the phthalone is converted into the *compound* $C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH{\cdot}C_{11}H_8N$, which crystallises from alcohol in red needles and melts at 135°; the *hydrochloride* melts at 176—178°, the *mercurichloride* at 98°, and the *benzoyl* derivative, $C_6H_4<\begin{matrix}CH_2\\CH(OBz)\end{matrix}>CH{\cdot}C_{11}H_8N$, forms small, white leaflets and melts at 155°. 6-*Phenylpyrophthaline*,

$$C_6H_4<\begin{matrix}CO\\C(NH)\end{matrix}>CH{\cdot}C_{11}H_8N,$$

prepared by heating 6-phenylpyrophthalone with alcoholic ammonia for 7—8 hours at 200°, crystallises from alcohol in red leaflets and melts above 307°.

N-*Ethyl*-6-*phenylpyrophthaline* melts at 194°, and gives a *platinichloride* which melts and decomposes at 225°.

N-n-*butyl*-6-*phenylpyrophthaline* melts at 168°, and its *platinichloride* at 194°, and N-*benzyl*-6-*phenylpyrophthaline* melts at 211°. N-*Mesityl*-6-*phenylpyrophthaline*, prepared from the phthalone and mesidine, forms thick crystals melting at 230°. W. A. D.

A New Class of Coloured Dithiourethanes. JULIUS VON BRAUN (*Ber.*, 1903, 36, 3520—3527. Compare Abstr., 1902, i, 271).—*Piperidyl*-S-*benzoyldithiourethane*, $C_5H_{10}N{\cdot}CS{\cdot}SBz$, obtained by shaking an aqueous solution of piperidine or piperidyldithiocarbamate with benzoyl chloride (compare Abstr., 1903, i, 13), separates from alcohol in lustrous, yellow crystals and melts at 85—90°; when kept in a sealed vessel for several days or boiled with alcohol for 2—3 minutes, it is converted by loss of carbon disulphide into benzoyl piperidine, which boils at 320—321°, and not at 360° as stated by Schotten (Abstr., 1888, 1105). *Piperidyl*-p-*anisoyldithiourethane*, $C_5H_{10}N{\cdot}CS{\cdot}S{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$, prepared similarly by using anisic chloride in place of benzoyl chloride, crystallises from alcohol and has a deep yellow colour; it melts at 62—65° and is more stable at the ordinary temperature than the benzoyl derivative, although when boiled with alcohol it readily gives *anisoylpiperidine*,

$$C_5H_{10}N{\cdot}CO{\cdot}C_6H_4{\cdot}OMe,$$

as a yellow oil boiling at 220—222° under 14 mm. pressure.

N-*Dimethyl*-S-*benzoyldithiourethane*, $NMe_2{\cdot}CS{\cdot}SBz$, melts at 59° and is very unstable, being readily transformed into dimethylbenzamide. *Dimethyl*-p-*anisoyldithiourethane* is a yellow substance melting at 78—80°.

Attempts to prepare a urethane from diethylamine diethyldithiocarbamate and phenylacetyl chloride gave a deep yellow solution which rapidly became colourless owing to the formation of *phenylacetodiethylamide*, $CH_2Ph{\cdot}CO{\cdot}NEt_2$, which boils at 167—168° under 15 mm. pressure; the urethane formed from propionyl chloride and dipropylamine dipropyldithiocarbamate is equally unstable and is at once resolved into *dipropylpropionamide*, $C_2H_5{\cdot}CO{\cdot}NPr_2$, which boils at 107—108° under 16 mm. or at 227° under the ordinary pressure.

Ethyl chlorocarbonate gives with piperidine piperidyldithiocarbamate the urethane, $C_5H_{10}N{\cdot}CO_2Et$, and with dipropylamine dipropyldithiocarbamate, dipropylurethane, $NPr_2{\cdot}CO_2Et$ (Abstr., 1902, i, 610). Ethylamine ethyldithiocarbamate and benzoyl chloride, however, give the *thiourethane*, $NHEt{\cdot}CS{\cdot}SBz$, which forms slightly yellow crystals, melts at 76°, and is comparatively stable at the ordinary temperature; when boiled with alcohol, it forms ethylbenzamide.

N-*Phenyl*-S-*benzoyldithiourethane* crystallises from alcohol, melts at 64°, and is highly coloured; when boiled with alcohol, it forms phenylbenzamide.

Benzoyldithiourethane, $NH_2{\cdot}CS{\cdot}SBz$, obtained from ammonium dithiocarbamate and benzoyl chloride, crystallises from alcohol, melts at 108—109°, and easily affords benzamide.

The bright yellow colour of all these substances is emphasised, and its relationship with that shown by other sulphur compounds (Abstr., 1903, i, 618—619) discussed. W. A. D.

Action of Chloralammonia on Ethyl Disodiomalonate. RUDOLF ZWERGER (*Monatsh.*, 1903, **24**, 737—746).—The action of chloralammonia on ethyl disodiomalonate leads to the formation of a substance which is considered to be *diethyl* 2 : 6-*dihydroxy*-1 : 4-*dihydropyridine*-4 : 4-*dicarboxylate*, $NH<\begin{matrix}C(OH){:}CH\\C(OH){:}CH\end{matrix}>C(CO_2Et)_2$ (compare Guthzeit, Abstr., 1894, i, 71). The ester crystallises in delicate needles containing $\frac{1}{2}H_2O$, melts at 195—196°, is easily soluble in hot water, absolute alcohol, or ether, and gives an intense red coloration with ferric chloride. The *sodium* derivative, $C_{11}H_{14}O_6NNa,2H_2O$, crystallises in silky needles and loses $2H_2O$ at 105°; the *barium* derivative, $C_{22}H_{28}O_{12}N_2Ba,2H_2O$, forms delicate needles; the *silver* derivative forms a white precipitate of microscopic needles. G. Y.

Condensation of Ethyl Cyanoacetate with Cinnamaldehyde and Piperonaldehyde. GALEAZZO PICCININI (*Atti R. Accad. Torino*, 1903, **38**, 894—921. Compare Carrick, Abstr., 1892, 1086, and Guareschi, Abstr., 1900, i, 52, and 1902, i, 819).—The condensation of ethyl cyanoacetate with cinnamaldehyde in presence of ammonia yields: (1) the 2-*ammonium* derivative of hydrostyryldicyanoglutaconimide [3 : 5-dicyano-2-hydroxy-4-β-phenylethyldihydro-6-pyridone], $CH_2Ph{\cdot}CH_2{\cdot}C<\begin{matrix}C(CN){\cdot}CO\text{———}\\CH(CN){\cdot}C(ONH_4)\end{matrix}>N$, which separates from aqueous alcohol as a white, crystalline mass melting and decomposing at 215—220°, and is only decomposed by concentrated hydrochloric acid on heating, when it evolves ammonia; (2) ethyl styrylcyanoacrylate, in small quantity.

The condensation of ethyl cyanoacetate with piperonaldehyde in presence of ammonia gives:

(1) the *ammonium* derivative of 3 : 5-dicyano-2-hydroxy-4-piperonyldihydro-6-pyridone, $C_{14}H_{10}O_4N_4$, which crystallises from aqueous alcohol in long, white needles soluble in water; it is unstable and becomes coloured at the ordinary temperature, evolves ammonia at 70—80°, and melts at above 300°. Its aqueous solution gives precipitates with silver nitrate, mercurous nitrate, copper acetate, barium or calcium chloride, &c. 3 : 5-*Dicyano*-2-*hydroxy*-4-*piperonyldihydro*-6-*pyridone*,

$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3{\cdot}C<\begin{matrix}C(CN){\cdot}CO\text{———}\\CH(CN){\cdot}C(OH)\end{matrix}>N,$$

separates from a mixture of alcohol and ether in crystals, which are soluble in aqueous acetone or aqueous acetic acid, become brown at 150—180°, and melt at above 300°. The aqueous solution gives precipitates with many inorganic salts, including potassium chloride (1 in 800 solution), and with various alkaloids, including nicotine hydrochloride (a 1 in 16,000 solution is precipitated after a time). The *nicotine* derivative, $C_{10}H_4N_2,2C_{14}H_7O_4N_3$, separates in needles which contain $\frac{1}{2}H_2O$ and turn brown at 250°, and melt and decompose at about 290°. The derivatives of the following metals were prepared and analysed: *silver*, *barium* ($+4H_2O$), *calcium* ($+5H_2O$), *copper*, and *cobalt*.

(2) *a-Cyano-β-piperonylpropionamide*,

$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3{\cdot}CH_2{\cdot}CH(CN){\cdot}CO{\cdot}NH_2,$$

which separates from alcohol in white crystals melting at 186—186·5°; it has a neutral reaction, and is soluble in water or acetone, showing in the latter a normal ebullioscopic behaviour; when boiled with barium hydroxide in a current of steam, it gives off ammonia (2 mols.).

(3) *α-Cyano-β-piperonylideneacetamide*,

$$CH_2{<}^{O}_{O}{>}C_6H_3{\cdot}CH{:}C(CN){\cdot}CO{\cdot}NH_2,$$

separating from aqueous alcohol in bright yellow crystals which melt at 209° and evolve ammonia when boiled with barium hydroxide in a current of steam; when treated with bromine, it does not yield an additive product, but a *bromo*-derivative,

$$CH_2{<}^{O}_{O}{>}C_6H_2Br{:}C(CN){\cdot}CO{\cdot}NH_2,$$

which is deposited from alcohol in slender, yellow crystals, turning brown at 235° and melting at 245°. T. H. P.

Pyridine Bismuth Chloride. OTTO HAUSER and LUDWIG VANINO (*Ber.*, 1903, **36**, 3682—3684).—The formula, $2BiCl_3,3C_5H_5N$, previously (Abstr., 1901, i, 289) assigned to the precipitated salt is confirmed (compare Montemartini, Abstr., 1901, i, 163; 1903, i, 111).

J. J. S.

Asymmetric Nitrogen. ALBERT LADENBERG (*Ber.*, 1903, **36**, 3694—3699).—The following experiments are adduced to prove the existence of *iso*stilbazoline.

l-*Stilbazoline a-tartrate* crystallises in large prisms, not very sharply formed, melting at 78—80°. At 13°, 100 parts of water dissolve 14·5 parts of the salt. The corresponding base has $[\alpha]_D$ $-9·44°$. By heating stilbazoline, it is converted into a base boiling at 156—158° under a pressure of 20 mm. and having $[\alpha]_D$ $-6·3°$ to $-6·46°$. The *tartrate* formed from this crystallises easily, and 100 parts of water dissolve about 14 parts. On the other hand, the tartrate prepared from a mixture of the *l*- and *i*-bases, having a specific rotation of about $-6·5°$, only crystallised after a long interval, and 100 parts of water dissolved more than 50 parts. E. F. A.

Constitution and Optical Behaviour of the Nitrosoalkylurethanes and of Anthranil. JULIUS W. BRÜHL (*Ber.*, 1903, **36**, 3634—3645. Compare Abstr., 1902, i, 353).—The refractometric determinations made by O. Schmidt (Abstr., 1903, i, 681) with nitrosoalkylurethanes and anthranil have been repeated by the author, who confirms Schmidt's conclusions as to the constitution of nitrosoalkylurethanes, but agrees with Bamberger, in opposition to Schmidt, as to the constitution of anthranil (compare following abstract).

Nitrosoalkylurethanes are true nitrosoamines; the values previously quoted by Brühl (Abstr., 1897, ii, 297) are too high, as the compounds examined were impure. Nitrosoethylurethane boils at 77° under 19 mm. pressure [Schmidt gives 69—70° under 15 mm. pressure] n_D 1·43968; sp. gr. 1·0885 at 16·9°/4°; $\mathfrak{M}_D$ 35·33 (Schmidt finds 35·12). Nitrosomethylurethane boils at 67—67·5° under 14 mm. pressure; $n_D = 1·44196$; sp. gr. 1·1402 at 19°/4°; $\mathfrak{M}_D$ 30·63

(Schmidt finds 30·66). Since the spectrochemical values for the grouping N_2O in nitrosoalkylamines and nitrosoalkylurethanes (nitrosoacylamines) vary only within the limits of experimental error, the constitution of nitrosoalkylurethanes may be regarded as settled.

From his optical determinations Schmidt regards anthranil as having the constitution $C_6H_4{<}\substack{CO\\ |\\ NH}$, as against Bamberger's $C_6H_4{<}\substack{CH\\ |\\ N-}{>}O$. The author points out that Schmidt's figures do not bear out his conclusion, since the value for the molecular refraction is much smaller than it should be, if the former constitution is correct.

The constitution of methylanthranil has been definitely settled by Bamberger, who synthesised it from *o*-nitroacetophenone (Abstr., 1903, i, 432, 560). Comparison of the refractometric values of anthranil and methylanthranil indicate the correctness of Bamberger's anthranil formula. Anthranil boils at 93—93·5° under 9 mm. pressure; n_D 1·58609; sp. gr. 1·1827 at 19·8°/4°; $\mathfrak{M}_D$ 33·77 (calculated = 33·156). Methylanthranil boils at 115·5—116° under 11 mm. pressure; n_D 1·57967; sp. gr. 1·1334 at 19·95°/4°; $\mathfrak{M}_D$ 39·04 (calculated = 37·759). A. McK.

Anthranil. VIII. Eugen Bamberger and Franz Elger (*Ber.*, 1903, **36**, 3645—3658. Compare Abstr., 1902, i, 127, 95, 650; 1903, i, 84, 432, 417, 560; also preceding abstract).—Bamberger and his pupils have shown that *o*-amino-aromatic aldehydes and ketones can be oxidised to anthranil derivatives, thus:

$$C_6H_4{<}\substack{NH_2\\ COR} \longrightarrow \left(C_6H_4{<}\substack{NH\cdot OH\\ COR}\right) \longrightarrow C_6H_4{<}\substack{N-\\ |\\ CR-}{>}O + H_2O.$$

This is not, however, a general reaction for substances of the type $C_6H_4(NH_2)COR$, since anthranilic acid (or methyl anthranilate) is oxidised by Caro's acid to *o*-nitrosobenzoic acid (or methyl *o*-nitrosobenzoate) and not to hydroxyanthranil (or methoxyanthranil). If the intramolecular dehydration of the hypothetical intermediate hydroxylamine derivative takes place, thus:

$$<\substack{NH\cdot OH\\ CO\cdot R} \longrightarrow <\substack{N-\\ |\\ CR}{>}O,$$

more quickly than its oxidation, thus: $<\substack{NH\cdot OH\\ CO\cdot R} \longrightarrow <\substack{NO\\ CO\cdot R}$, then an anthranil is formed; if the oxidation takes place more rapidly than the dehydration, a nitroso-compound is obtained.

It is now shown that *o*-nitrobenzaldehydedimethylacetal, *o*-nitrobenzaldehyde, and *o*-nitroacetophenone, when carefully reduced, can be converted into the corresponding hydroxylamine derivatives, which, in the presence of hydrogen ions, undergo transformation with such extreme ease into anthranils that it was found impossible to isolate them. *o*-Aminoacetophenone and *o*-aminobenzophenone, when oxidised by Caro's acid, yield methylanthranil and phenylanthranil respectively.

When *o*-nitrobenzaldehydedimethylacetal, $NO_2\cdot C_6H_4\cdot CH(OMe)_2$, is reduced by aluminium amalgam, it forms *o*-hydroxylaminobenzaldehyde dimethylacetal, $OH\cdot NH\cdot C_6H_4\cdot CH(OMe)_2$, the aqueous solution of which quickly becomes turbid on exposure to air (in the same manner as

an aqueous solution of phenylhydroxylamine), reduces Fehling's solution in the cold, and interacts with diazonium chloride to form a substance giving the ferric chloride coloration characteristic of benzeneazohydroxyanilide. Addition of a drop of dilute hydrochloric acid to the aqueous solution of this hydroxylamine compound causes the immediate formation of anthranil. The reduction of *o*-nitrobenzaldehydediethylacetal by ammonium chloride and zinc dust proceeds in an analogous manner.

When *o*-nitrobenzaldehyde is reduced by aluminium amalgam, it yields anthranil with the intermediate formation of *o*-hydroxylaminobenzaldehyde. Similarly, *o*-nitroacetophenone yields methylanthranil with the intermediate formation of *o*-hydroxylaminoacetophenone, which was detected by its action on Fehling's solution, &c.

By reduction of *o*-nitrobenzaldoxime with ammonium chloride and zinc dust, an almost theoretical yield of *o*-hydroxylaminobenzaldoxime may be obtained (compare Bamberger and Demuth, Abstr., 1902, i, 95). The latter is oxidised by a current of air to *o-azoxybenzaldoxime*, $ON_2(C_6H_4{\cdot}CH{:}N{\cdot}OH)_2$, and anthranil; dilute acid also decomposes it to form hydroxylamine and anthranil, thus:

$$OH{\cdot}NH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OH = C_6H_4{<}{\overset{N}{\underset{CH}{}}}{>}O + NH_2{\cdot}OH.$$

A. McK.

Syntheses in the *iso*Quinoline Series. II. Attempts to Synthesise Papaverine. PAUL FRITSCH (*Annalen*, 1903, 329, 37—65. Compare Abstr., 1895, i, 624).—Starting from 3 : 4 : 3′ : 4′-tetramethoxydeoxybenzoin, the synthesis of papaverine has been attempted; this compound was condensed with acetalamine, when the substance

$$CH(OEt)_2{\cdot}CH_2{\cdot}N{:}C[C_6H_3(OMe)_2]{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$$

was formed, which yielded a very small quantity of an alkaloid isomeric with papaverine; the melting point, however, was considerably higher than that of papaverine.

Diveratryldichloroethane, $CHCl_2{\cdot}CH[C_6H_3(OMe)_2]_2$, is prepared by condensing veratrole with dichloroacetal by means of 72·5 per cent. sulphuric acid; the product is poured on to ice and the solid which separates after treatment with water and cold alcohol, dissolved in warm alcohol, whence the condensation product separates in lustrous prisms melting at 122°; on treatment with alcoholic potassium hydroxide, it is converted into *diveratrylchloroethylene*,

$$CHCl{:}C[C_6H_3(OMe)_2]_2,$$

which crystallises in colourless needles melting at 98° and is soluble in sulphuric acid with an intense reddish-violet coloration. *Tetramethoxytolane*, $C_2[C_6H_3(OMe)_2]_2$, is obtained from this compound by heating it under pressure with a solution of potassium in amyl alcohol for 2 hours at 175—180°; from the solid product of the reaction, the unchanged material was extracted by means of ether, in which the tolane is but little soluble; the tolane, the yield of which never exceeds 45 per cent. of the theoretical, crystallises in colourless prisms melting at 156°, and dissolves in sulphuric acid with an intense violet coloration. The *dibromide*, $C_2Br_2[C_6H_3(OMe)_2]_2$, crystallises in leaflets melting at 208°.

Many attempts were made to prepare the tetramethoxydeoxybenzoin from the tolane derivative; it was finally obtained by dissolving the tolane in mercaptan saturated with hydrogen chloride and treating the product thus formed with ether and hydrogen chloride; the deoxybenzoin crystallises from alcohol in needles melting at 108° and is soluble in sulphuric acid, no coloration appearing. The mercaptol, $C_6H_3(OMe)_2 \cdot C(SEt) \colon CH \cdot C_6H_3(OMe)_2$, is doubtless formed as an intermediate product and can be isolated under certain conditions; it is an oil boiling at 190—200° under 15 mm. pressure.

Tetramethoxydeoxybenzoinoxime,

$$C_6H_3(OMe)_2 \cdot C(\colon NOH) \cdot CO \cdot C_6H_3(OMe)_2,$$

is prepared by adding an alcoholic solution of sodium containing amyl nitrite to a solution of the deoxybenzoin in benzene, and then extracting the solution with dilute alkali hydroxide; it crystallises in colourless leaflets melting at 149—150°. *Tetramethoxybenzil* was obtained from the last mentioned compound by treating its solution in acetic acid with sodium nitrite, and crystallises in yellow needles or prisms melting at 219—220°. This substance was also prepared from the dimethyl ether of vanillin by treatment of its alcoholic solution with potassium cyanide and subsequent oxidation of the benzoin, which was not isolated, with ammoniacal copper oxide. The identity of the two substances demonstrates the correctness of the constitution of tetramethoxydeoxybenzoin, above given.

Tetramethoxydeoxybenzoinacetalamine is prepared by slowly adding acetalamine to the deoxybenzoin, which is heated in a special apparatus in a stream of dry hydrogen at 200—210°; it is a viscous, yellowish-brown oil, and is immediately decomposed into its constituents by water. When distilled under a pressure of 0·35 mm., a red oil passes over at 255—265°, which is probably a vinyl derivative, formed from the acetalamine by loss of alcohol,

$$OEt \cdot CH \colon CH \cdot N \colon C[C_6H_3(OMe)_2] \cdot CH_2 \cdot C_6H_3(OMe)_2.$$

Since papaverine can be recovered without loss from a solution in 80 per cent. sulphuric acid, whilst only about 30 per cent. can be recovered from a solution in 85 per cent. sulphuric acid, the conversion of the acetalamine derivative into the alkaloid was attempted by treatment with 75 per cent. sulphuric acid; a base, $C_{20}H_{21}O_4N$, was obtained which crystallised in pale yellow leaflets melting at 162° (papaverine melts at 147°), but resembling the alkaloid in other respects.

The author discusses the syntheses in the *iso*quinoline series in the light of the recent work of Rügheimer (Abstr., 1903, i, 438).

K. J. P. O.

The Acetylenic Ketones. New Method of Synthesising *iso*Oxazoles. CHARLES MOUREU and M. BRACHIN (*Compt. rend.*, 1903, **137**, 795—797).—By the action of hydroxylamine on acetylphenylacetylene, ($CPh \colon C \cdot COMe$), in aqueous alcoholic solution, 5-phenyl-3-methyl*iso*oxazole, $O<\begin{matrix} N = CMe \\ CPh \colon CH \end{matrix}$, is formed; it melts at 68° (Goldschmidt, Abstr., 1895, i, 529, gives 65°) and boils at 151—152° under 19 mm. pressure.

Propionylphenylacetylene, $CPh \cdot C \colon C \cdot COEt$, prepared by the action of

propionyl chloride on the sodium derivative of phenylacetylene, boils at 137—138° under 16 mm. pressure, melts at 8—10°, has a sp. gr. 1·0043 at 23°/0°, and on treatment with hydroxylamine yields 5-*phenyl*-3-*ethyl*iso*oxazole*, $O<\begin{matrix}N = CEt \\ CPh:CH\end{matrix}$, which boils at 157—158° under 18 mm. pressure, melts at about −2°, and has a sp. gr. 1·0766 at 18°/0°; it dissolves in concentrated hydrochloric acid and is reprecipitated by water.

Butyrylphenylacetylene, CPh·C:C·COPr, obtained by the condensation of the sodium derivative of phenylacetylene and butyryl chloride, boils at 148—150° under 18 mm. pressure, and has a sp. gr. 0·9859 at 23°/0°; it reacts with hydroxylamine to form 5-*phenyl*-3-*propyl*iso*oxazole*, $O<\begin{matrix}N = CPr \\ CPh:CH\end{matrix}$, which boils at 168—169° under 18 mm. pressure, melts between 5° and 10°, and has a sp. gr. 1·0536 at 18°/0°; it dissolves in concentrated hydrochloric acid and is reprecipitated by water.

3:5-Diphenyl*iso*oxazole, $O<\begin{matrix}N = CPh \\ CPh:CH\end{matrix}$, formed from benzoylphenylacetylene, crystallises from alcohol, is slightly soluble in ether, and insoluble in concentrated hydrochloric acid. It melts between 142° and 190°, giving off a gas at 170°; the resolidified product melts between 140° and 146° (Goldschmidt, Abstr., 1896, i, 189, gives 141° as the melting point of this compound).

3-*Anisyl*-5-*phenyl*iso*oxazole*, $O<\begin{matrix}N = C\cdot C_6H_4\cdot OMe \\ CPh:CH\end{matrix}$, formed from anisoylphenylacetylene and hydroxylamine, crystallises from methyl alcohol in thin, white needles, melts at 128—129°, and is insoluble in concentrated hydrochloric acid.

The formation of these *iso*oxazoles takes place in two phases, (1) CPh:C·COMe + NH_2·OH = H_2O + CPh:C·CMe:N·OH, and (2) the acetylenic oxime changes into the isomeric *iso*oxazole, $O<\begin{matrix}N = CMe \\ CPh:CH\end{matrix}$.

M. A. W.

Diacid Quaternary Ammonium Bases: Ethylenedikairolinium Iodide. EDGAR WEDEKIND (*Ber.*, 1903, **36**, 3796—3801. Compare Abstr., 1903, i, 517).—Kairoline and ethylene iodide unite to form a tertiary compound, the hydriodide of 1-methyltetrahydroquinoline, decomposing at 164—165°, as chief product, as well as small quantities of a quaternary iodide melting at 265—266°. *Ethyleneditetrahydroquinoline*, $C_9NH_{10}\cdot CH_2\cdot CH_2\cdot C_9NH_{10}$, prepared by heating a mixture of tetrahydroquinoline (4 mols.) and ethylene bromide (1 mol.) at 100°, crystallises from alcohol in colourless needles melting at 146—147°. Heating with an excess of methyl iodide converts this into *ethylenedikairolinium iodide*, $C_2H_4(C_9NH_{10}MeI)_2$, which forms colourless needles melting and decomposing at 206°; it is therefore probably isomeric with the quaternary iodide just described. The d-*camphorsulphonate* forms colourless crystals which melt at a higher temperature than the iodide does.

E. F. A.

The Two Phenylhydrazinoacetic Acids. MAX BUSCH, SEBASTIAN SCHNEIDER, and AUGUST WALTER (*Ber.*, 1903, 36, 3877—3890. Compare Elbers, Abstr., 1885, 534; Reissert and Kayser, 1891, 1054; Reissert, 1895, i, 460; Harries, *ibid.*, 459).—A mixture of the ethyl esters of *s*- and *as*-phenylhydrazinoacetic acids is obtained by the condensation of ethyl chloroacetate and phenylhydrazine by Reissert's method. When the condensation takes place between the acid and phenylhydrazine in the presence of an alkali hydroxide, the only product is Harries' *as*-phenylhydrazinoacetic acid. The two isomeric acids may be separated by the addition of an aqueous solution of oxalic acid, the *s*-acid remains undissolved as it is less basic, whereas the *as*-acid forms a soluble oxalate. s-*Phenylhydrazinoacetic acid*, $NHPh\cdot NH\cdot CH_2\cdot CO_2H$, crystallises in colourless, glistening plates, begins to turn brown at 170°, and melts and decomposes at 172—173°. It is only sparingly soluble in alcohol or water and is practically insoluble in ether or benzene. On treatment with ammoniacal copper solutions, it yields the phenylhydrazone of glyoxylic acid and no nitrogen is evolved. The *hydrochloride* of the hydrazino-acid melts and decomposes at about 165°, the hydrochloride of the ester has only been obtained as an oil. The *oxalate* of the ester may be obtained by the addition of an ethereal solution of the ester to a solution of oxalic acid in the same solvent.

as-Phenylhydrazinoacetic acid yields a hydrochloride melting and decomposing at about 170°, a benzylidene derivative melting at 165—166°, and a m-*nitrobenzylidene* compound,

$$NO_2\cdot C_6H_4\cdot CH:N\cdot NPh\cdot CH_2\cdot CO_2H,$$

melting at 196—197°. The hydrochloride of the ethyl ester may be obtained by passing hydrogen chloride into an alcoholic solution of the acid and is readily soluble in warm water (compare Harries.) The corresponding *oxalate* melts at 126° and is readily soluble in cold water, and the m-*nitrobenzylidene* derivative crystallises in small yellow needles and melts at 86°.

Ethyl α-phenylsemicarbazido-α-acetate,

$$NH_2\cdot CO\cdot NH\cdot NPh\cdot CH_2\cdot CO_2Et,$$

obtained by the action of potassium cyanate on an aqueous solution of the ethyl ester of the *as*-acid, crystallises from hot water in compact crystals melting at 123° and readily soluble in alcohol. On hydrolysis with aqueous sodium hydroxide, it yields *α-phenylsemicarbazido-α-acetic acid*, melting at 190—191°, but with alcoholic potash yields *phenyldiketohexahydro*-1 : 2 : 4-*triazine*, $NPh<\begin{matrix}NH\cdot CO\\CH_2\cdot CO\end{matrix}>NH$, which crystallises from hot water in iridescent, thin plates melting at 225°. It has the properties of a feeble acid and dissolves in sodium hydroxide solution, but not in ammonia. When boiled with alkali, the ring is ruptured and the phenylcarbazidoacetic acid is formed.

Ethyl cyanate and ethyl *as*-phenylhydrazinoacetate yield *ethyl α-phenyl-δ-ethylsemicarbazido-α-acetate*, $NHEt\cdot CO\cdot NH\cdot NPh\cdot CH_2\cdot CO_2Et$, which forms transparent, flat prisms melting at 97—98°. The corresponding acid melts at 195°, and 1-*phenyl*-4-*ethyldiketohexahydro*-1 : 2 : 4-*triazine* at 135—136°.

Ethyl αδ-diphenylsemicarbazido-α-acetate forms small, colourless

needles, readily soluble in alcohol or benzene and melting at 160°, the corresponding *acid* crystallises in either needles or plates melting and decomposing at 203—204°. A triazine derivative has not been obtained.

aδ-Diphenylthiosemicarbazide-a-acetic acid,

$$NHPh\cdot CS\cdot NH\cdot NPh\cdot CH_2\cdot CO_2H,$$

obtained from the ethyl ester (compare Harries, *loc. cit.*), crystallises in colourless needles and melts and decomposes at 195°. When the ethyl ester is digested with cold alcoholic potash, a mixture of the free acid and of a yellow compound, $NPh{:}C{<}{\genfrac{}{}{0pt}{}{NH\cdot NPh}{S\text{———}CO}}{>}CH_2$, melting and decomposing at 201° is obtained. This yellow compound may readily be separated from the acid, as it is insoluble in sodium carbonate solution. It is also sparingly soluble in the ordinary solvents. Carbonyl chloride reacts with ethyl *as*-phenylhydrazinoacetate yielding an oil, $CO_2Et\cdot CH_2\cdot NPh\cdot NH\cdot COCl$, and *ethyl diphenylcarbazidodiacetate*, $CO(NH\cdot NPh\cdot CH_2\cdot CO_2Et)_2$, in the form of colourless prisms softening at 114—115° and decomposing at a higher temperature. The *acid* melts and decomposes at 235° and is only sparingly soluble in alcohol or glacial acetic acid. The ester, on treatment with cold alcoholic potash yields a soluble *acid*, $CO_2H\cdot CH_2\cdot NPh\cdot N{<}{\genfrac{}{}{0pt}{}{CO\cdot CH_2}{CO\cdot NH}}{>}NPh$, melting at 176°, together with the acid melting at 235°. J. J. S.

Hydrazones derived from *p*-Nitrophenylhydrazine and *p*-Dinitrodibenzylhydrazine. William Alberda van Ekenstein and Jan J. Blanksma (*Rec. trav. chim.*, 1903, 22, 434—439. Compare Bamberger and Kraús, Abstr., 1896, i, 610; 1899, i, 666, and Hyde, Abstr., 1899, i, 688).—When dextrose (2 grams) dissolved in alcohol (30 c.c.) is warmed for ten minutes at 100° with *p*-nitrophenylhydrazine (2 grams) and the liquid evaporated to dryness in a desiccator, there is formed a *dextrose*-p-*nitrophenylhydrazone*, which crystallises in yellow needles, melts at 185°, and has $[a]_D + 21\cdot5°$ in pyridine. When acetic acid is employed as the solvent, there is formed a second *dextrose*-p-*nitrophenylhydrazone*, which separates from alcohol in yellow crystals, melts at 195°, and has $[a]_D - 128\cdot7°$. This modification is also produced by solution of the form melting at 185° in acetic acid. From both forms, the same osazone is readily obtained by the further action of *p*-nitrophenylhydrazine in presence of acetic acid (Hyde, *loc. cit.*).

Mannose-p-*nitrophenylhydrazone*, similarly prepared, also exists in two forms, the one (produced in presence of methyl alcohol) forming yellow crystals and melting at 190°, the other (produced in presence of acetic acid) melting at 202°.

The following *p*-nitrophenylhydrazones of other sugars have been prepared: *lævulose*-p-*nitrophenylhydrazone* melts at 176° and has $[a]_D + 16°$; *galactosephenylhydrazone* melts at 192° and has $[a]_D + 45\cdot6°$; *xylose*-p-*nitrophenylhydrazone* melts at 156°, *rhamnose*-p-*nitrophenylhydrazone* melts at 186° and has $[a]_D + 48\cdot3°$, whilst *arabinose*-p-*nitrophenylhydrazone* melts at 168° and has $[a]_D + 48\cdot3°$. Maltose and lactose do not react with *p*-nitrophenylhydrazine in presence of alcohol.

From these *p*-nitrophenylhydrazones, the sugars are readily regenerated by warming with benzaldehyde, when the *p*-nitrophenylhydrazone of the latter is formed, melting at 190° (compare Hyde, *loc. cit.*). The corresponding *derivatives* of *o*-nitrobenzaldehyde, *p*-tolualdehyde, and salicylaldehyde melt respectively at 250°, 198°, and 225°.

The author has also prepared the p-*dinitrodibenzylhydrazones* of the following substances; the melting points of these are given in brackets: dextrose (142°), galactose (153°), lævulose (112°), *o*-nitrobenzaldehyde (120°), *p*-tolualdehyde (163°), and salicylaldehyde (183°).

It is suggested that *p*-nitrophenylhydrazine may be employed for the detection of acetone in alcohol denatured with wood spirit, and in urine. Diethyl ketone and methyl ethyl ketone, which may also occur in wood spirit, furnish p-*nitrophenylhydrazones*, melting respectively at 141° and 128°. T. A. H.

Action of Iodine on Benzaldehydephenylhydrazone in Pyridine Solution. GIOVANNI ORTOLEVA (*Gazzetta*, 1903, 33, ii, 51—60).—The action of iodine on benzaldehydephenylhydrazone in pyridine solution results in the formation of: (1) diphenyldibenzylidenehydrotetrazone, (2) dehydrobenzaldehydephenylhydrazone, and (3) a *compound*, $C_{18}H_{18}N_3I$, which crystallises from alcohol in yellow needles melting at 265—267°, and is soluble in water, acetic acid, acetic anhydride, or dilute hydrochloric acid, from the last two of which it separates unchanged after boiling; when boiled with alkalis, it is completely resinified and evolves a basic odour similar to that of pyridine; from its aqueous solution, silver nitrate completely precipitates the iodine, whilst with mercuric chloride it gives a *double* salt, $C_{18}H_{18}N_3I,3HgCl_2,H_2O$, which separates from water in white needles melting at 202—204°; when heated with dilute nitric acid, it yields a *base*, which separates from a mixture of chloroform and ether in slender, white needles melting at 214—215° and yields, with mercuric chloride, a *compound* separating from water in white needles melting at 219—220°, whilst its *platinichloride*, $(C_{18}H_{17}N_3)_2,H_2PtCl_6$, melts and decomposes at 238—239°; the same platinichloride is obtained from the original compound, $C_{18}H_{18}N_3I$, and from the compound obtained by the action of dilute hydrochloric acid on the latter. T. H. P.

Condensation of Oximes with Hydrazines and the Properties of Hydrazones. CHARLES REUTT and BRONISLAS PAWLEWSKI (*Bull. Acad. Sci. Cracow*, 1903, 502—504).—The authors have attempted to prepare compounds of the type R·CH:N·NH·NHR′ by condensing aldoximes with hydrazines, but have obtained instead the corresponding hydrazones of the aldehydes (compare Just, Abstr., 1886, 701).

Benzaldehydephenylhydrazone, produced by the condensation of benzaldoxime with phenylhydrazine, melts at 158—160° and decomposes when heated at 100—110°. The red *modification* produced by the exposure of this to light melts at the same temperature and is reconverted into the colourless form at 115—120° or by preservation in the dark.

*Benzaldehyde-*o*-tolylhydrazone,* $CHPh:N·NH·C_6H_4Me$, produced in small quantity by condensing benzaldoxime with *o*-tolylhydrazine,

forms golden-yellow needles, melts at 100—102°, and is converted by the action of light into a red *form* which melts at 80—83°.

Benzaldehyde-p-*tolylhydrazone*, similarly prepared, forms short, sand-coloured needles, melts at 114°, and becomes red on exposure to light, the melting point falling at the same time to 101°. T. A. H.

Action of Phenylcarbimide on Amino-acids. Carl Paal and Georg Zitelmann (*Ber.*, 1903, 36, 3337—3345).—*Phenylureidosuccinic monoamide*, $NHPh\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NH_2$, formed by the addition of phenylcarbimide to a solution of *l*-asparagine in sodium hydroxide, forms colourless prisms and melts at 164°. It is dextrorotatory, having $[\alpha]_D$ $+21\cdot66°$ at 16°, where $p=8\cdot7$ and $d=1\cdot040$. Its *barium* and *silver* salts are described.

By the action of phenylcarbimide on a solution of *l*-aspartic acid in sodium hydroxide, a mixture of phenylureidosuccinic acid and its anhydride, γ-phenylhydantoin-α-acetic acid, is formed. When this mixture is heated with dilute sodium hydroxide solution or with baryta water and the resulting solution then acidified by hydrochloric acid, *phenylureidosuccinic acid*, $NHPh\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, separates in colourless crystals which melt at 183°. It may also be formed from phenylureidosuccinic monoamide or from γ-phenylhydantoin-α-acetic acid. It has $[\alpha]_D$ $+5\cdot70°$ at 16°, where $p=10\cdot82$ and $d=1\cdot069$. Its *barium* and *silver* salts are described. The acid very readily parts with water to form *γ-phenylhydantoin-α-acetic acid*, $CO{<}\begin{matrix}NPh\cdot CO\\ NH-CH\cdot CH_2\cdot CO_2H\end{matrix}$, which may also be formed by heating phenylureidosuccinic monoamide with hydrochloric acid. It crystallises from water in colourless prisms or needles which melt at 228°; its *sodium* salt has $[\alpha]_D$ $-52\cdot05°$ at 16°, where $p=8\cdot52$ and $d=1\cdot043$. Its *ethyl* ester separates from alcohol in colourless leaflets and melts at 122°.

2-*Phenylureidoethanesulphonic acid*, $NHPh\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot SO_3H$, prepared from phenylcarbimide and taurine, separates in colourless, tiny needles and decomposes at 175°. Its *barium* salt crystallises with $1\frac{1}{2}H_2O$. The acid does not form an anhydride when heated with hydrochloric acid, acetic anhydride, or acetyl chloride.

β-p-*Hydroxyphenyl-α-phenylureidopropionic acid*,

$$NHPh\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH,\tfrac{1}{2}H_2O,$$

prepared from phenylcarbimide and tyrosine, melts at 104°. Its *barium* salt contains $6H_2O$ and its *silver* salt $1H_2O$. When warmed with dilute sulphuric acid, the acid forms *α*-p-*hydroxybenzyl-γ-phenylhydantoin*, $CO{<}\begin{matrix}NPh\cdot CO\\ NH-CH\cdot CH_2\cdot C_6H_4\cdot OH\end{matrix}$, which separates from water in colourless needles and melts at 184°. A. McK.

Chrysean. Gustaf Hellsing (*Ber.*, 1903, 36, 3546—3553. Compare Abstr., 1899, i, 563; 1900, i, 518).—The following facts show that chrysean is either *4-aminothiazole-2-carbothioamide*, $S{<}\begin{matrix}CH{=\!=\!=}C\cdot NH_2\\ C(CS\cdot NH_2){:}N\end{matrix}$, or the corresponding *μ-amino*iso*thiazole-α-carbothioamide*.

Chrysean methiodide, $C_4H_5N_3S_2$, obtained by interaction of chrysean with methyl iodide in alcoholic solution, crystallises from alcohol in slender, yellowish-brown needles, and commences to decompose at 180°. The *formyl* derivative, $C_4H_3N_2S_2\cdot NH\cdot CHO$, prepared by boiling chrysean with anhydrous formic acid, crystallises from alcohol in golden spangles and decomposes at 210°. The *benzoyl* derivative, $C_4H_3N_2S_2\cdot NHBz$, forms small, yellowish-brown needles and melts at 212—213°.

The substance melting at 216°, which was previously described (*loc. cit.*) as 1-acetyl-4 : 4-dimethyl-2 : 6-dicyanodihydrodithiazine, is in reality the *diacetyl* derivative, $S<\begin{matrix}CH{=\!=\!=\!=}C\cdot NAc_2\\ C(CS\cdot NH_2){:}N\end{matrix}$, of chrysean, and can be obtained by boiling this substance with acetic anhydride alone. The compound formed by heating chrysean with aqueous silver sulphate is, moreover, not a dicyanodihydroazthiotetride, but *aminocyanothiazole*, $S<\begin{matrix}CH{=\!=}C\cdot NH_2\\ C(CN){:}N\end{matrix}$; with benzaldehyde, it gives the *benzylidene* derivative, $CN\cdot C_3NSH\cdot N{:}CHPh$, which crystallises from alcohol in small, yellowish-white needles and melts at 140—141°.

Acetylaminothiazolecarboxylamide, $NHAc\cdot C_3NSH\cdot CO\cdot NH_2$, prepared by the action of hydrogen peroxide on the corresponding nitrile ("acetyldicyanodihydroazthiotetride"), crystallises in small, six-sided plates and decomposes above 250°; *acetylaminothiazolecarboxylic acid*, $NHAc\cdot C_3NSH\cdot CO_2H$, obtained by hydrolysing the amide, melts and decomposes at 166°, and gives a *sodium* salt crystallising in white needles and a *methyl* ester which melts and decomposes at 178°. *Acetylaminothiazole*, $C_3NSH_2\cdot NHAc$, prepared by decomposing the carboxylic acid at 170—180°, crystallises from alcohol, benzene, or water both with and without solvent of crystallisation and melts at 162°.

When aminocyanothiazole and its acetyl derivative are caused to combine with hydrogen sulphide in alcoholic solution, they give rise respectively to chrysean and acetylchrysean. W. A. D.

Reduced Derivatives of 4-Phenylpyrazole. *cis*-1-Phenyl-*trans*-2 : 3-trimethylenedicarboxylic Acid. EDWARD BUCHNER and LASAR PERKEL (*Ber.*, 1903, 36, 3774—3782).—4-*Phenylpyrazoline*, $NH<\begin{matrix}N{=\!=}CH\\ CH_2\cdot CHPh\end{matrix}$, prepared by heating ethyl 4-phenylpyrazolinedicarboxylate (from ethyl cinnamate and ethyl diazoacetate) with hydrochloric acid, is an oil which oxidises very readily in air to phenylpyrazole. It does not lose nitrogen when heated at 230—240°, but is partially converted into 4-phenylpyrazole and hydrogen. The hydrochloride melting at 162° has already been described (Abstr., 1893, i, 282), the *platinichloride* is very unstable and melts at 116—117°. The *aurichloride* is a yellow precipitate which decomposes without melting when heated. The *oxalate* separates from alcohol in white crystals and melts at 120°.

Ethyl 4-*phenylpyrazolidine*-3 : 5-*dicarboxylate*,

$$CHPh<\begin{matrix}CH(CO_2Et)\cdot NH\\ CH(CO_2Et)\cdot NH\end{matrix},$$

prepared by reducing the pyrazoline ester with zinc dust and acetic acid, boils at 280° without decomposition, crystallises from ether in colourless needles, and melts at 91°. The *acid* crystallises from boiling water in colourless needles, melts at 227—228°, does not immediately decolorise alkaline permanganate, is not acted on by bromine, and does not lose carbon dioxide when heated with hydrochloric acid; the benzyl derivative crystallises from alcohol and melts and decomposes at 280°, but it was not analysed.

The *nitro*-derivative, $NO_2{\cdot}C_6H_4{\cdot}C_3H_3(CO_2H)_2$, of *cis*-1-phenyl-*trans*-2 : 3-trimethylenedicarboxylic acid (Abstr., 1892, 849) separates from water in colourless needles and melts with slight decomposition at 245°. The *amino*-derivative, $NH_2{\cdot}C_6H_4{\cdot}C_3H_3(CO_2H)_2$, forms colourless crystals which become brown at 220°, but do not melt at 300°; the *hydrochloride* forms colourless needles and melts and decomposes at 198°; the *hydrochloride* of the *dimethyl* ester crystallises from methyl alcohol and melts and decomposes at 204°. The amino-derivative is oxidised by permanganate to trimethylene-*trans*-1 : 2 : 3-tricarboxylic acid,

$$C_3H_3(CO_2H)_3,$$

thus establishing the position of the phenyl group; the relative positions of the two carboxyl groups in the phenyl compound had already been determined by conversion into an anhydride. An isomeric acid, probably cis-1-*phenyltrimethylene*-cis-trans-2 : 3-*dicarboxylic acid* is produced by fusing the *trans*-acid with potassium hydroxide at 230—240°; it separates from boiling water in colourless needles, melts at 121°, and is stable towards aqueous permanganate.

T. M. L.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. Robert Stollé (*J. pr. Chem.*, 1903, [ii], 68, 417—424. Compare Abstr., 1903, i, 721).—The action of acid chlorides on the silver derivatives of the condensation products of aldehydes or ketones with acylhydrazides leads to the formation of additive compounds (Minunni and Satta, Abstr., 1900, i, 251), which by elimination of silver chloride pass over into substituted dihydrodiazoles.

By this reaction, there have been prepared 4-*benzoyl*-2 : 5-*diphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*oxadiazole*, $N\!\!<\!\!\begin{array}{l}NBz{\cdot}CHPh\\ \quad\;\; | \\ CPh{\cdot}O\end{array}$, from the silver derivative of benzylidenebenzhydrazone and benzoic chloride; 4-*acetyl*-2 : 5-*diphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*oxadiazole*, which melts at 53°, from benzylidenebenzhydrazone and acetic chloride; 4-*benzoyl*-5-*phenyl*-2-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*oxadiazole*, which melts at 98°, from benzylideneacethydrazone and benzoic chloride; 4-*acetyl*-5-*phenyl*-2-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*oxadiazole*, from benzylideneacethydrazone and acetic chloride; and 4-*benzoyl*-2 : 5 : 5-*triphenyl*-4 : 5-*dihydro*-1 : 2 : 4-*oxadiazole*, from benzophenonebenzhydrazone and benzoic chloride.

These dihydro-oxadiazoles are crystalline, stable solids and are easily soluble in alcohol, but less so in ether. When boiled with a few drops of hydrochloric acid in ethereal solution, they are hydrolysed with formation of diacylhydrazides, but in aqueous solution with formation of the products of hydrolysis of these.

G. Y.

Derivatives of Pyrimidine and Methylated Pyrimidines. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1903, 36, 3379—3385. Compare Büttner, this vol., i, 658).—The chlorodimethoxypyrimidine, melting at 73°, described by Büttner is reduced by zinc dust and fuming hydrochloric acid in alcoholic solution to a 2 : 6-*dimethoxypyrimidine*, which boils at 204·5—205°, solidifies at 10°, is miscible with water, gives a white, crystalline double salt, $2C_6H_8O_2N_2,3HgCl_2$, with mercuric chloride, and forms an *aurichloride*, $C_6H_8O_2N_2,HAuCl_4$, melting at 139·5°. When heated on the water-bath with strong hydrochloric acid, it is converted into uracil, thus establishing its constitution, as also that of Büttner's compound, as 4-*chloro*-2 : 6-*dimethoxypyrimidine.*

4-*Chloro*-2-*amino*-6-*methoxypyrimidine*, which melts at 168—169°, can be obtained either from 4 : 6-dichloro-2-aminopyrimidine by heating it with methyl alcohol and sodium or by acting on Büttner's dichloromethoxypyrimidine, melting at 51°, with methyl-alcoholic ammonia. Büttner's base is therefore 2 : 4-*dichloro*-6-*methoxypyrimidine.*

2-*Amino*-6-*methoxypyrimidine*, formed by reducing the above substance, boils at 274°, crystallises from ethyl acetate in quadratic plates melting at 118·5—120°, is soluble in warm water with an alkaline reaction, and forms a *platinichloride*, $(C_5H_7ON_3)_2,H_2PtCl_6$, which sinters at 236° but is not melted at 270°. 2-Amino-6-hydroxypyrimidine, prepared by evaporating the preceding base with concentrated hydrochloric acid, crystallises in microscopic cubes and octahedra melting at 276—277°, and is identical with the base prepared synthetically by Wheeler and Johnson (Abstr., 1903, i, 526). 6-*Chloro*-2-*aminopyrimidine* is formed when the preceding compound is boiled with phosphorus oxychloride; it sinters and becomes brown at 168°.

4-Methylpyrimidine condenses with benzaldehyde in presence of zinc chloride to form 4-*styrylpyrimidine*, $N{<}{\substack{CH{:}CH \\ CH{-\!-}N}}{>}C{\cdot}CH{:}CHPh$, which boils at 325—327°, crystallises from light petroleum in plates melting at 72—74°, and forms a *dibromide*, $C_{12}H_{10}N_2Br_2$, crystallising from alcohol in brownish-yellow, oblong plates, which melt and decompose at 225—226°. 2 : 4-Dimethylpyrimidine condenses with benzaldehyde in similar manner to form 2 : 4-*Distyrylpyrimidine*, which crystallises in colourless needles melting at 145—146°. E. F. A.

Conversion of Phthalazine into Pyridazine Derivatives. SIEGMUND GABRIEL (*Ber.*, 1903, 36, 3373—3378).—Chloro-opiazine, $C_6H_2(OMe)_2{<}{\substack{CH{:}N \\ CCl{:}N}}$, which is best prepared from opiazone by heating it with phosphorus oxychloride, when reduced with hydrogen iodide, has both halogen and methyl replaced by hydrogen, forming 7 : 8-*dihydroxyphthalazine*, the *hydrochloride* of which crystallises in yellow needles; the *platinichloride* and the sparingly soluble *picrate* melting at 197° were also prepared. When oxidised with permanganate, this is converted into pyridazine-4 : 5-dicarboxylic acid, $\begin{matrix} N{:}CH{\cdot}C{\cdot}CO_2H \\ | \qquad\quad \| \\ N{:}CH{\cdot}C{\cdot}CO_2H \end{matrix}$, which sinters at 205° and melts and decomposes at 212—213·5°; this is

identical with the acid obtained by Täuber on heating pyridazinetetracarboxylic acid. In a similar manner, phthalazine can be oxidised to the same acid.

4-*Iodophthalazine*, $C_6H_4<\begin{matrix}CH:N \\ CI=N\end{matrix}$, formed by heating 4-chlorophthalazine with hydrogen iodide, crystallises in stellar aggregates of needles and melts at 78° to a reddish-brown mass. E. F. A.

Terpenes and Ethereal Oils. Transformation of Cyclic Ketones into Pyrazole Bases. OTTO WALLACH [with AD. STEINDORFF] (*Annalen*, 1903, 329, 109—133).—With the exception of the preparation of phenylpyrazole from hydroxymethylenecamphor by Claisen, the formation of pyrazoles from cyclic ketones has not been studied. A series of pyrazoles has been obtained in which five-, six-, and seven-membered carbon rings are linked with the simple pyrazole ring. Further unsubstituted pyrazoles, which have not hitherto been prepared, have been obtained.

The cyclic hydroxymethyleneketones, for example,

$$CH_2<\begin{matrix}CH_2\cdot CO \\ CH_2\cdot C:CH\cdot OH\end{matrix},$$

yield a semicarbazone, which in some instances can be isolated, but generally loses water, forming the compound (carbamide of a pyrazole or cyclic semicarbazone), $CH_2<\begin{matrix}CH_2\cdot C=N \\ CH_2\cdot C:CH\end{matrix}>N\cdot CO\cdot NH_2$. On hydrolysis with dilute acids, carbon dioxide and water are eliminated and the pyrazole obtained, $CH_2<\begin{matrix}CH_2\cdot C=N \\ CH_2\cdot C:CH\end{matrix}>NH$. The same pyrazoles can also be obtained directly from the hydroxymethylene compounds by the action of hydrazine, but they cannot be so easily purified when thus prepared.

The carbamide derivatives of the pyrazoles (cyclic semicarbazones) are crystalline insoluble substances, which can be used to recognise the presence of hydroxymethylene compounds.

Although two isomeric semicarbazones of a cyclic hydroxymethylene are possible, only one has been observed; the heterocyclic carbamide of the pyrazoles appears to exist in two forms, both of which yield the same pyrazole on hydrolysis, as they exhibit a double melting point in many cases.

The polycyclic pyrazoles are crystalline and very feebly basic; they yield precipitates with mercuric chloride and silver nitrate.

The *hydroxymethylene* derivative of *cyclo*pentanone is prepared by adding sodium to a mixture of amyl nitrite and *cyclo*pentanone, and forms white crystals melting at 72—73°; it only reacts with semicarbazide in the presence of sulphuric acid, giving a semicarbazone melting at 175—177°. When boiled with dilute sulphuric acid, it is converted into a pyrazole which melts at 57—59°.

From 1:3-methyl*cyclo*pentanone, a *hydroxymethylene* derivative is prepared which melts at 53—54° and boils at 105—112° under 22 mm. pressure; its cyclic *semicarbazone*, $C_8H_{11}ON_3$, melts at 115—116°, and when treated with dilute acids yields an oily pyrazole.

*Hydroxymethylene*cyclo*hexanone*, prepared from *cyclo*hexanone, is an oil boiling at 98—100° under 55 mm. pressure; its cyclic *semicarbazone*, $C_8H_{11}ON_3$, melts at 183—184° or at 220°, and yields the *pyrazole*,

$$\begin{array}{l} CH_2\cdot CH_2\cdot C{=}N \\ | \qquad\qquad\quad | \\ CH_2\cdot CH_2\cdot C{:}CH \end{array}\!\!>NH,$$

which forms crystals melting at 84°.

The *hydroxymethylene* derivative of 1 : 3-methyl*cyclo*hexone is an oil boiling at 85° under 12 mm. pressure, and readily yields a cyclic *semicarbazone*, which melts at 154—157°. The *pyrazole*, $C_8H_{11}N_2$, prepared either from the semicarbazone or by the action of hydrazine on the hydroxymethylene derivative, melts at 99—100°; the *hydrochloride* is very soluble and the *picrate* is a yellow, crystalline powder melting at 136—138°; the silver nitrate *compound*, $(C_8H_{12}N_2)_2,AgNO_3$, crystallises from methyl alcohol and melts at 137—139°.

The *semicarbazone*, $C_{12}H_{21}O_3N_3$, obtained from hydroxymethylenementhone, melts at 167—169° and passes into the *carbamide* of the pyrazole (cyclic semicarbazole), $C_{12}H_{19}ON_3$, which has the melting points 117—118° and 143—144°. The *menthonepyrazole*, $C_{11}H_{18}N_2$, is an oil and yields a *platinichloride* melting at 216°.

Hydroxymethylenetetrahydrocarvone is a pale yellow liquid boiling at 131—135° under 16 mm. pressure; with semicarbazide, it yields the carbamide of the pyrazole, $C_{12}H_{19}ON_3$, which melts at 150° and not sharply at 178—182°, and is hydrolysed by dilute sulphuric acid to the *pyrazole*, $C_{11}H_{18}N_2$; this base is an oil and gives a *platinichloride* melting at 226—228°.

Hydroxymethylenedihydrocarvone yields a *semicarbazone* melting at 163—165°, which is converted by sulphuric acid into the *carbamide* of the pyrazole (the cyclic semicarbazone); the latter melts at 125—127° and then solidifies to melt again at 146—148°. The *pyrazole*, $C_{11}H_{16}N_2$, is an oil, the *platinichloride* of which melts at 201°.

Hydroxymethylenethujone reacts with semicarbazide in acetic acid solution to form a *monosemicarbazone*, $C_{12}H_{19}O_2N_3$, which melts at 179—181°; it is converted by sulphuric acid in acetic acid solution into the cyclic *compound*, $C_{12}H_{10}ON_3$, melting at 133—134°. The *pyrazole*, $C_{11}H_{16}N_2$, is an oil and gives a *platinichloride* melting at 188—190°.

*Hydroxymethylene*iso*thujone*, which is an oil boiling at 128—132° under 18 mm. pressure, yields a *semicarbazone*, $C_{12}H_{19}O_2N_3$, melting at 204—205°; it readily passes into the cyclic *compound*, $C_{12}H_{17}ON_3$, melting at 193—194°, with elimination of water. From either by the action of sulphuric acid, the *pyrazole*, $C_{11}H_{16}N_2$, melting at 89—90°, can be prepared; its *platinichloride* melts at 220—222°.

Hydroxymethylenethujamenthone, an oil boiling at 109—115° under 11 mm. pressure, reacts slowly with semicarbazide, forming a *semicarbazone*, $C_{12}H_{21}O_2N_3$, which melts at 125—145°; the cyclic *compound*, $C_{12}H_{19}ON_3$, has a double melting point 121—122°, and 159—161°. The *pyrazole*, $C_{11}H_{18}N_2$, is a liquid.

Hydroxymethylenesuberone, $C_8H_{12}O_2$, is a liquid boiling at 100° under 10 mm. pressure, and when acted on by semicarbazide yields directly the cyclic *compound*, $C_9H_{13}ON_3$, which melts at 181—183°. The

pyrazole, $CH_2<\begin{array}{l}CH_2\cdot CH_2\cdot C{=}N\\ CH_2\cdot CH_2\cdot C{:}CH\end{array}>NH$, melts at 66—67° and yields a *platinichloride* melting at 238—239°.

Hydroxymethylenecamphor behaves like the compound last mentioned and gives first a *semicarbazone*, $C_{12}H_{19}O_2N_3$, melting at 217—218°, which then loses water, the cyclic *compound*, $C_{12}H_{17}ON_3$, melting at 150° and then at 205—207°, being produced. The *pyrazole* of camphor, $C_8H_{14}<\begin{array}{l}C{:}CH\\ C{=}N\end{array}>NH$ or $C_8H_{14}<\begin{array}{l}C{-}CH\\ C\cdot NH\end{array}>N$, melts at 149—150°.

Behaviour of the Hydroxymethylene Derivatives of Acyclic Ketones towards Semicarbazide.—The hydroxymethylene derivative of acetone alone reacts with semicarbazide to form a *disemicarbazone*, $C_6H_{11}O_2N_6$, which melts at 232°. When boiled with acids, it passes into *methylpyrazole*, $C_4H_6N_2$, which melts at 240°. The hydroxymethylene derivative of methyl ethyl ketone gives directly a cyclic *compound*, $C_6H_9ON_3$, which melts and decomposes at 164—165°. When boiled with dilute sulphuric acid, it yields 4 : 5-*dimethylpyrazole*, melting at 55—57°. K. J. P. O.

Action of Carbon Disulphide on Hydrazo-compounds. PAUL JACOBSON and A. HUGERSHOFF [and, in part, EDW. JANKOWSKI and W. LISCHKE] (*Ber.*, 1903, 36, 3841—3857).—Hydrazo-compounds react more readily with carbon disulphide than azo-derivatives; with hydrazo-compounds, the reaction takes place readily at 150° and proceeds according to one or other of the two schemes (*a*) $NHR\cdot NHR + CS_2 = NHR\cdot CS\cdot NHR + S$, whereby a diarylated thiocarbamide and free sulphur are obtained; (*b*) with *p*-hydrazophenol ethers, $C_{14}H_{16}ON_2 + CS_2 = C_{15}H_{14}ON_2S + H_2S$, whereby cyclic compounds of the type of 2-thiol-6-ethoxy-1-phenylbenziminazole, $SH\cdot C<\begin{array}{l}NPh\\ N\end{array}>C_6H_3\cdot OEt$, are produced. A considerable amount of the hydrogen sulphide is used up in the reduction of the hydrazino-compounds to primary amines, which can then react with the carbon disulphide yielding open chain thiocarbamides. The yield of benziminazole compound is never more than 35 per cent. owing to these secondary reactions, and even when an excess of the azo-compound is introduced into the original mixture in order to react with the hydrogen sulphide and generate hydrazo-compounds, the yield is not improved.

s-Diphenylthiocarbamide, di-*p*-tolylthiocarbamide, di-*o*-tolylthiocarbamide, and phenyl-*o*-tolylthiocarbamide melting at 140°, have been obtained from the corresponding hydrazo-compounds.

2-Thiol-6-ethoxy-1-phenylbenziminazole (Jacobson and Fischer, Abstr., 1892, 839), obtained from Bohn's benzenehydrazophenetole melting at 86° by the action of carbon disulphide at the ordinary temperature, or better at 150°, crystallises in long, felted needles, melts at 229°, is not hydrolysed by alkalis, and on treatment with mercuric oxide yields a *compound*, $Hg(C_{15}H_{13}ON_2S)_2$, and with acetic anhydride and sodium acetate an *acetyl* derivative melting at 163—164°.

2-*Thiol*-6-*ethoxy*-1-p-*tolylbenziminazole*, obtained from Noelting and

Werner's *p*-tolylhydrazophenetole (Abstr., 1891, 211), crystallises in colourless needles, melts at 205—206°, and yields an *acetyl* derivative melting at 145°. A secondary product is p-*tolyl*-p-*phenetylthiocarbamide*, melting at 134—135°.

Benzenehydrazo-m-*cresetole*, $NHPh\cdot NH\cdot C_6H_3Me\cdot OEt$, forms colourless crystals melting at 100°, and with carbon disulphide at 150° yields 2-*thiol*-6-*ethoxy*-1-*phenyl*-4-*methylbenziminazole*, melting at 244—245° and sparingly soluble in alcohol. No acetyl derivative could be obtained.

Toluene-o-*hydrazo*-m-*cresetole*, $C_6H_4Me\cdot NH\cdot NH\cdot C_6H_3Me\cdot OEt$, melting at 80°, yields 2-*thiol*-6-*ethoxy*-1-o-*tolyl*-4-*methylbenziminazole*, melting at 240°.

3 : 4-Dimethyl-4 ethoxyhydrazobenzene (compare Noelting and Werner, *loc. cit.*) yields with carbon disulphide 2-thiol-6-ethoxy-1-*p*-tolyl-5-methylbenziminazole, melting at 205—206° and identical with the compound obtained by the action of carbon disulphide on 2-amino-5-ethoxy-4 : 4′-dimethyldiphenylamine (Jacobson and Schwartz, Abstr., 1896, i, 26). A secondary product is di-*p*-tolylthiocarbamide.

Toluene-*p*-hydrazo-*p*-cresetole (Noelting and Werner, *loc. cit.*) melts at 55°, not at 153°, and with carbon disulphide at 160° yields p-*tolyl*-p-*cresetylthiocarbamide*, $C_6H_4Me\cdot NH\cdot CS\cdot NH\cdot C_6H_3Me\cdot OEt[Me_2:OEt = 4:3':6']$, melting at 158°. J. J. S.

Chromophore Groupings. I. Methineammonium Dyes. HANS RUPE and A. PORAI-KOSCHITZ (*Zeit. Farb. Text.-Chem.*, 1903, 2, 449—453. Compare Abstr., 1902, i, 40).—o-*Nitrobenzylidene*-2-*methylbenziminazole* [2-o-*nitrostyrylbenziminazole*],

$$C_6H_4{<}^{NH}_{N}{>}C\cdot CH{:}CH\cdot C_6H_4\cdot NO_2,$$

prepared by heating 2-methylbenziminazole with *o*-nitrobenzaldehyde for ¾ hour at 185—195°, crystallises from dilute alcohol in yellowish-green leaflets and melts at 215°; on reduction with stannous chloride and hydrochloric acid, it gives 2-o-*aminostyrylbenziminazole*, which crystallises from dilute alcohol in colourless needles, melts at 213°, and rapidly oxidises in the air; the *acetyl* derivative, $C_{17}H_{15}ON_3$, forms large needles and melts at 285°.

2-m-*Nitrostyrylbenziminazole* forms white needles decomposing at 220° and is unstable; the *hydrochloride* forms white needles. 2-m-*Aminostyrylbenziminazole*, $C_{15}H_{13}N_3,\frac{1}{2}H_2O$, crystallises from dilute alcohol or acetic acid in white needles and melts at 116° losing its water of crystallisation, the anhydrous substance subsequently melting at 153°; the *hydrochloride*, $C_{15}H_{13}N_3,2HCl$, crystallises in stellate aggregates of needles, and the *platinichloride*, $C_{15}H_{13}N_3,H_2PtCl_6$, forms white needles.

2-p-*Nitrostyrylbenziminazole* crystallises from alcohol and melts and decomposes at 269—270°; it is extraordinarily sensitive to oxidation and could not be obtained pure; the *hydrochloride* crystallises from dilute alcohol in white needles. 2-p-*Aminostyrylbenziminazole*, $C_{15}H_{13}N_3,H_2O$, melts at 225° and cannot be recrystallised; the *hydrochloride*, $C_{15}H_{13}N_3,2HCl$, forms orange-red, and the *sulphate*

$C_{15}H_{13}N_3,H_2SO_4$, yellow needles; the *acetyl* derivative, $C_{17}H_{15}ON_3$, has a high melting point.

The azo-compounds derived from 2-*p*-aminostyrylbenziminazole dye cotton directly faster shades than the azo-compounds derived from the corresponding *m*-amino-compound, whilst these are faster than the *o*-amino-dyes. It is noteworthy that the para- and ortho-aminostyrylbenziminazoles can, in the form of their salts with mineral salts, dye silk and wool, whilst the meta-bases entirely lack this property. It is suggested that the ortho- and para-compounds owe their tinctorial power to the possibility of their forming coloured quinonoid salts of the type

$$C_6H_4{<}{\overset{NH}{\underset{N}{—}}}{\geqslant}C{\cdot}CH_2{\cdot}CH{:}C_6H_4{:}NH_2Cl,$$

whilst the meta-derivative,

$$C_6H_4{<}{\overset{NH}{\underset{N}{—}}}{\geqslant}C{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NH_2,HCl,$$

is colourless. W. A. D.

Researches on Azo-compounds. New Mode of Formation of Indazole Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1903, **137**, 982—984. Compare Abstr., 1903, i, 584).—*o*-Hydrazobenzoic acetal decomposes in neutral solution into methyl alcohol and *o-indazylbenzylacetal*, $C_6H_4{<}{\overset{N—}{\underset{CH}{|}}}{>}N{\cdot}C_6H_4{\cdot}CH(OMe)_2$, which, on further warming, is partially transformed into *o-indazylbenzaldehyde*, $C_6H_4{<}{\overset{N—}{\underset{CH}{|}}}{>}N{\cdot}C_6H_4{\cdot}CHO$, which crystallises from ether in long, white needles and melts at 94·5—95°. It dissolves in boiling nitric acid without oxidation; on cooling, the *nitrate* crystallises in needles decomposed by water. The *hydrazone* crystallises in small, yellow prisms melting and decomposing at 191°.

o-Azobenzaldehyde is almost instantly decolorised by warming with 10 per cent. sulphuric acid, forming *o*-indazylbenzoic acid, together with a small quantity of a substance not yet identified.

C. H. D.

3 : 5-Dibromo-2-aminobenzoic Acid and its Nitrile. Synthesis of Quinazolines. MARSTON T. BOGERT and WILLIAM F. HAND (*J. Amer. Chem. Soc.*, 1903, **25**, 935—947).—*o*-Aminobenzonitrile (Bogert and Hand, Abstr., 1903, i, 292) is converted into 3 : 5-*dibromo-2-aminobenzonitrile* by bromination with a solution of bromine in carbon tetrachloride, benzene, or water, by alkaline potassium hypobromite, or, preferably with an acidified solution of potassium bromide and bromate. It separates from alcohol in small, white, feathery needles and melts at 156—156·5° (corr.). It does not form a salt when hydrogen chloride is passed into its ethereal solution, neither does it form an acetyl compound when boiled with acetic anhydride. When hydrolysed, it forms 3 : 5-*dibromo-2-aminobenzoic acid*, crystallising from alcohol in white needles and melting at

235·6—236° (corr.). This acid can be conveniently prepared by brominating anthranilic acid with a mixture of potassium bromide and bromate in presence of hydrochloric acid. When heated at 260—270°, it decomposes with evolution of hydrogen bromide. Its *barium* salt is sparingly soluble in cold water and crystallises with $2H_2O$. By elimination of the amino-group from 3 : 5-dibromo-2-aminobenzoic acid, 3 : 5-dibromobenzoic acid is formed, the barium salt of which crystallises with $3\frac{1}{2}H_2O$.

The elimination of the amino-group from 3 : 5-dibromo-2-aminobenzonitrile takes place with great difficulty, and the yield of 3 : 5-dibromobenzoic acid is very small.

When 3 : 5-dibromo-2-aminobenzonitrile is heated with formic acid at 225—235°, it forms 6 : 8-*dibromo*-4-*ketodihydroquinazoline*,

CH·CBr·C—N:CH
CBr·CH·C·CO·NH (compare Bogert and Hand, *loc. cit.*; Bogert, Breneman, and Hand, Abstr., 1903, i, 527). It crystallises in small needles and decomposes above 300°. Its *ethyl ether* separates from alcohol in snow-white needles and melts at 229—230° (corr.).

6 : 8-*Dibromo*-2-*methyl*-4-*ketodihydroquinazoline*, prepared by heating the nitrile with acetic anhydride at 220—230°, separates from aniline in snow-white crystals which begin to decompose at 300°. Its *ethyl ether* begins to decompose at about 170°.

6 : 8-*Dibromo*-2-*ethyl*-4-*ketodihydroquinazoline*, prepared from the nitrile and propionic anhydride, crystallises from dilute alcohol in silky needles and melts at 278—280° (corr.).

6 : 8-*Dibromo*-2-n-*propyl*-4-*ketodihydroquinazoline* crystallises from dilute alcohol in colourless, microscopic needles and melts at 238—240° (corr.).

6 : 8-*Dibromo*-2-iso*propyl*-4-*ketodihydroquinazoline* melts at 259—260° (corr.).

6 : 8-*Dibromo*-2-iso*butyl*-4-*ketodihydroquinazoline* forms colourless, microscopic needles and melts at 230—231·5° (corr.).

6 : 8-*Dibromo*-2-*methyl*-4-*thioketodihydroquinazoline*, prepared by heating 3 : 5-dibromo-2-aminobenzonitrile with thioacetic acid at 220—230°, crystallises from aniline in yellow needles and does not melt at 290°. Its *ethyl ether* forms light yellow needles and begins to decompose at about 305°. A. McK.

Indanthrene and Flavanthrene. I. Roland Scholl (*Ber.*, 1903, **36**, 3410—2426, 3710. Compare Hinsberg, Abstr., 1902, i, 238).—Indanthrene A, *N*-dihydro-1 : 2 : 2′ : 1′-anthraquinonazine (following abstract), differs from most of the other derivatives of dihydrophenazine in its remarkable stability, and shows very little tendency to undergo oxidation.

Its constitution follows from its method of formation, the para-position of the NH groups being deduced from the fact that it does not yield a diamine on reduction.

The paper contains a discussion on the constitution of indanthrene, and of the relationship between the constitution and the stability and colour of the compound. J. J. S.

Indanthrene and Flavanthrene. II. ROLAND SCHOLL and HANS BERBLINGER (*Ber.*, 1903, 36, 3427—3445. Compare Abstr., 1903, i, 446, 530, 582).—Indanthrene A, N-*dihydro*-1 : 2 : 1′ : 2′-*anthraquinonazine*, $C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{NH\\NH}>C_6H_2<\substack{CO\\CO}>C_6H_4$ (Abstr., 1902, i, 721), is obtained when β-aminoanthraquinone is fused at 250° for half an hour with 5 times its weight of potassium hydroxide and 1/5th of its weight of potassium nitrate. The product is boiled with water and the insoluble dye removed and reduced by treatment with sodium hydroxide and sodium hyposulphite at 60—70°. The sodium derivative is thus obtained in the form of well-developed needles with a coppery lustre, and when dissolved in water and oxidised by atmospheric oxygen is reconverted into indanthrene A. By this process, indanthrene B, which is also present, is removed.

Indanthrene A is practically insoluble in the usual organic solvents and is only very sparingly soluble in boiling aniline or nitrobenzene. It dissolves in hot quinoline (1 : 500), and the blue solution deposits blue needles with a coppery lustre somewhat resembling indigotin. When gently heated, it partly sublimes and is completely decomposed at 470—500°. It is only feebly basic, and its salts are readily decomposed by water.

When oxidised in concentrated sulphuric acid solution with nitric or chromic acid, it yields *anthraquinonazine*,

$$C_6H_4<\substack{CO\\CO}>C_6H_2{\ll}\substack{N\\N}>C_6H_2<\substack{CO\\CO}>C_9H_4,$$

which, on crystallisation from hexachlorobenzene or from nitrobenzene, forms greenish-yellow, flat prisms or hexagonal plates. Its salts with strong acids are slowly hydrolysed by water. The *sulphate*,

$$C_{28}H_{12}O_4N_2,H_2SO_4,$$

forms spindle-shaped rhombohedra. The base is readily reconverted into indanthrene even by simply heating with solvents of high boiling point containing hydrogen, for example, quinoline, phenol, or even nitrobenzene. When transferred to cotton fabrics, it is slowly reduced, probably at the expense of the cellulose. Indanthrene combines with anthraquinonazine to yield a compound of the type of quinhydrone. This is termed *anthraquinonazhydrine*, $C_{56}H_{26}O_8N_4$, and is formed as an intermediate product in the oxidation of indanthrene or in the reduction of anthraquinonazine. It crystallises in green, flat prisms, possesses only feebly basic properties, and is readily transformed, even during recrystallisation, into indanthrene.

A theoretical yield of 4-*chloroindanthrene*,

$$C_6H_4<\substack{CO\\CO}>C_6HCl<\substack{NH\\NH}>C_6H_2<\substack{CO\\CO}>C_6H_4,$$

is obtained when anthraquinonazine is boiled for 1 hour with concentrated hydrochloric acid. It crystallises from quinoline in deep blue needles. The technical product, indanthrene C (D.R.-P. 138167), obtained by the action of bromine at 60—80° on indanthreno dissolved in concentrated sulphuric acid, is a mixture of *di*- and *tri-bromoindanthrenes* which may be separated by crystallisation from quinoline.

4-*Aminoindanthrene*, obtained by the action of concentrated aqueous ammonia on anthraquinonazine at 200°, is a somewhat dirty blue

product. The corresponding *anilino*-compound has a deep purple blue colour.

Indanthrene, on reduction with hydriodic acid and red phosphorus, yields N-*dihydroanthranonazine*,

$$C_6H_4 < \genfrac{}{}{0pt}{}{CH_2}{CO} > C_6H_2 < \genfrac{}{}{0pt}{}{NH}{NH} > C_6H_2 < \genfrac{}{}{0pt}{}{CO}{CH_2} > C_6H_4,$$

in the form of a yellowish-brown powder; it is only sparingly soluble in the usual organic solvents, but dissolves in concentrated acids. It also dissolves in alcoholic solutions of alkalis yielding soluble salts of N-*dihydroanthranolazine*,

$$C_6H_4 < \genfrac{}{}{0pt}{}{CH—}{C(OH)} > C_6H_2 < \genfrac{}{}{0pt}{}{NH}{NH} > C_6H_2 < \genfrac{}{}{0pt}{}{C(OH)}{CH—} > C_6H_4.$$

Solutions of these alkali salts, when diluted with water, exhibit a greenish-yellow fluorescence. Between 334° and 344° (corr.), it decomposes into hydrogen and anthranonazine, and a similar but slower change occurs when it is boiled with nitrobenzene.

Anthranonazine, $C_6H_4 < \genfrac{}{}{0pt}{}{CO}{CH_2} > C_6H_2 \ll \genfrac{}{}{0pt}{}{N}{N} > C_6H_2 < \genfrac{}{}{0pt}{}{CH_2}{CO} > C_6H_4$, crystallises from nitrobenzene in brownish-red, prismatic needles with a green, metallic lustre. It begins to sublime at 360°, giving off a violet-red vapour. Its solutions are magenta-red in colour and exhibit no fluorescence. In the indanthrane, as in the anthracene series (Liebermann, Abstr., 1880, 665), fluorescence is only met with in those compounds having a *para*-linking joining the *meso*-carbon atoms. It dissolves in alcoholic alkalis yielding characteristic blue solutions of the metallic derivatives of anthranolazine. The addition of water to the blue solutions causes an immediate change of colour to red and the precipitation of anthranonazine.

1 : 2 : 2′ : 1′-*Anthrazine*, $C_6H_4 < \genfrac{}{}{0pt}{}{CH}{CH} > C_6H_2 \ll \genfrac{}{}{0pt}{}{N}{N} > C_6H_2 < \genfrac{}{}{0pt}{}{CH}{CH} > C_6H_4$, obtained by distilling indanthrene with zinc dust under reduced pressure, or by reducing the dye with hydriodic acid and red phosphorus at 210—220°, crystallises from nitrobenzene in brownish-yellow, prismatic needles. In dilute solutions, it exhibits a greenish-yellow fluorescence. It sublimes at about 340° and melts at about 390° (corr.), and is soluble in concentrated sulphuric or nitric acids. J. J. S.

Oxidation of Rosindone and Naphthaphenazine by Chromic Acid. OTTO FISCHER (*Ber.*, 1903, 36, 3622—3626).—The rosindonic acid, obtained by the oxidation of rosindone by chromic acid (Fischer and Hepp, Abstr., 1891, 1044), is shown not to be the primary product but to be produced by the transformation of the isomeric *iso*rosindonic acid.

When rosindone is oxidised by chromic acid and acetic acid, the temperature of the reaction not being allowed to exceed 70—80°, very little rosindonic acid is formed; the main product, iso*rosindonic acid*, dissolves in concentrated sulphuric acid to give a violet-red coloration, whilst rosindonic acid gives a deep yellow coloration. The *iso*-acid separates from a mixture of methylal and light petroleum in white prisms, which soften at 180° and melt at about 206° with evolution of

carbon dioxide. In contact with 10—15 parts of concentrated sulphuric acid, it undergoes transformation into the isomeric rosindonic acid in 10—15 minutes at the ordinary temperature, or in a few seconds if the mixture be gently warmed. Rosindonic acid crystallises from ethyl acetoacetate in plates and melts at 227—228°. The following formulæ probably represent rosindonic acid (I) and *iso*rosindonic acid (II) :

$$\text{I.}\quad C_6H_4\left\langle\begin{array}{l}C{:}N\text{———}C_6H_4\\ C\text{═══}NPh\\ C(CO_2H){\cdot}O\end{array}\right.\qquad \text{II.}\quad C_6H_4\left\langle\begin{array}{l}C{:}N\text{———}C_6H_4\\ C\text{═══}NPh.\\ C(OH){\cdot}CO{\cdot}O\end{array}\right.$$

When $\alpha\beta$-naphthaphenazine is oxidised by chromic acid, it forms $\alpha\beta$-diketonaphthaphenazine, which separates from a mixture of chloroform and light petroleum in needles and melts and decomposes at 265° (compare Lindenbaum, Abstr., 1901, i, 423). When the green solution obtained by dissolving $\alpha\beta$-diketonaphthaphenazine in sodium hydroxide is acidified with hydrochloric acid, *indenophenazineglycollic acid*, $C_6H_4<\begin{array}{l}N{:}C{\cdot}C_6H_4\\ N{:}C{\cdot}C(OH){\cdot}CO_2H\end{array}$, is formed ; this melts at 223—224°, and, like rosindonic acid, forms a yellow solution with concentrated sulphuric acid. A. McK.

Anilopyrine and 5-Anilino-1-phenyl-3-methylpyrazole. By August Michaelis and E. Hepner (*Ber.*, 1903, 36, 3271—3279. Compare Stolz, following abstract).—The substance considered by Michaelis and Gunkel (Abstr., 1901, i, 351) to be anilopyrine is in reality *5-anilino-1-phenyl-3-methylpyrazole*, $NPh<\begin{array}{l}C(NHPh){:}CH\\ N\text{═══}CMe\end{array}$; this is shown by the fact that it is obtained by heating propylantipyrine chloride, $NPh<\begin{array}{l}CCl\text{══}CH\\ NPrCl{:}CMe\end{array}$, with aniline at 200°, just as it is formed from antipyrine chloride (5-chloro-1-phenyl-3-methylpyrazole 2-methochloride) under similar conditions. The true *anilopyrine*, $NPh\left\langle\begin{array}{l}C\text{═══}CH\\ \quad >NPh\;|\\ NMe\text{═}CMe\end{array}\right.$, however, is obtained by heating antipyrine chloride with aniline (2 mols.) for 2 hours at 125° and decomposing the product with sodium hydroxide ; in these circumstances, the compound, $NPh<\begin{array}{l}C(NHPh){:}CH\\ NMeCl\text{═}CMe\end{array}$, initially formed, loses hydrogen chloride, and not methyl chloride as is the case at 200°. Anilopyrine can also be obtained from 5-anilino-1-phenyl-3-methylpyrazole by the action of sodium hydroxide on its methiodide,

$$NPh<\begin{array}{l}C(NHPh){:}CH\\ NMeI\text{══}CMe\end{array};$$

it melts at 58—59°, is strongly basic, and reduces warm solutions of silver salts. The *hydrochloride* is a white, crystalline, deliquescent substance. The *platinichloride*, $(C_{17}H_{17}N_3)_2,H_2PtCl_6$, forms thick, reddish-yellow crystals, melts at 203°, and is identical with the

platinichloride of 5-anilino-1-phenyl-3-methylpyrazole methochloride, $NPh<\begin{matrix}C(NHPh){:}CH\\ NMeCl=CMe\end{matrix}$; the analogous *aurichloride* crystallises in slender, reddish-yellow needles and melts at 125°. The *hydriodide* is identical with *5-anilino-1-phenyl-3-methylpyrazole 2-methiodide* and forms thick, white, lustrous crystals melting at 174°; the *picrate*, $C_{23}H_{20}O_6N_6$, melts at 170°, and the *dichromate*, $(C_{17}H_{17}N_3)_2,H_2Cr_2O_7$, at 185°.

Anilopyrine methiodide, $NPh<\begin{matrix}C(NMePh){:}CH\\ NMeI=CMe\end{matrix}$, formed with explosive violence by the union of the components, crystallises in rhombic plates and melts at 194°; the analogous *ethiodide*, $C_{19}H_{22}N_3I$, melts at 184—185° and the *propiodide* at 134°.

ψ-Anilopyrine (*5-methylanilino-1-phenyl-3-methylpyrazole*),

$$NPh<\begin{matrix}C(NMePh){:}CH\\ N=CMe\end{matrix},$$

is obtained by heating anilopyrine methiodide, when methyl iodide distils off, or by digesting antipyrine chloride with methylaniline at 200°; it crystallises from alcohol in slender, transparent crystals, melts at 88·5°, and boils at 220—228° under 20 mm. pressure. The *platinichloride*, $(C_{17}H_{17}N_3)_2,H_2PtCl_6$, forms slender, yellow needles and melts and decomposes at 208—212°; the methiodide is identical with the methiodide of anilopyrine. W. A. D.

5-Imino-1-phenyl-2:3-dimethylpyrine. FRIEDRICH STOLZ (*Ber.*, 1903, 36, 3279—3290).—The substance described by Michaelis and Gunkel (Abstr., 1901, i, 351) as iminopyrine is identical with Walther's 5-amino-1-phenyl-3-methylpyrazole (Abstr., 1897, i, 297). The true *iminopyrine* (5-imino-1-phenyl-2 : 3-dimethylpyrazolone), for which the author prefers the formula $NPh<\begin{matrix}C({:}NH)\cdot CH\\ NMe-CMe\end{matrix}$ analogous to Knorr's structure for antipyrine (compare Michaelis and Hepner, preceding abstract), is obtained by heating antipyrine chloride (5-chloro-1-phenyl-3-methylpyrazole 2-methochloride) with aqueous ammonia for 6 hours at 125—150° or with ammonium carbonate for 12 hours at 200°; it forms hygroscopic crystals, melts at 63°, is strongly basic, and rapidly absorbs carbon dioxide from the air, forming the *carbonate*, $C_{11}H_{13}N_3,H_2CO_3,H_2O$, which crystallises from alcohol in colourless prisms. *Iminopyrine hydrochloride*, $C_{11}H_{13}N_3,HCl$, separates from absolute alcohol in well-formed crystals and melts at 192°; the *platinichloride* melts at 207°, the *hydrobromide* at 196°, and the *picrate* at 191°. *Iminopyrine-ethylurethane*, $C_{11}H_{12}N_3\cdot CO_2Et$, prepared by shaking the carbonate with a solution of sodium hydroxide and ethyl chlorocarbonate, crystallises from alcohol in large prisms and melts at 178°.

Benzoyliminopyrine, $C_{18}H_{17}ON_3$, prepared by benzoylating iminopyrine, crystallises from dilute alcohol in striated prisms and melts at 176°. *Benzenesulphonyliminopyrine*, $C_{17}H_{17}N_3O_2S$, obtained by the interaction of the base with benzenesulphonic chloride, crystallises in prisms and melts at 211°.

5-*Methylimino*-1-*phenyl*-2 : 3-*dimethylpyrazolone*, obtained by heating iminopyrine with methyl iodide and methyl alcohol at 100—125°, or, preferably, by the interaction of methylamine and 5-chloro-1-phenyl-3-methylpyrazole 2-methochloride during 8 hours at 150°, gives a *picrate* which crystallises in lustrous, golden needles and melts at 131°; the *methiodide*, $C_{13}H_{18}N_3I$, crystallises from alcohol, on adding ether, in colourless needles, melts at 183°, and can also be obtained by heating iminopyrine carbonate with an excess of methyl iodide and methyl alcohol for 12 hours at 125°.

5-*Ethylimino*-1-*phenyl*-2 : 3-*dimethylpyrazolone*, prepared by heating antipyrine chloride with ethylamine at 125°, gives a *picrate* melting at 110°.

5-*Imino*-1-*phenyl*-2 : 3 : 4-*trimethylpyrazolone*, obtained by heating 5-chloro-1-phenyl-3 : 4-dimethylpyrazole-2-methochloride (Michaelis, Voss and Greiss, Abstr., 1901, i, 407) with aqueous ammonia for 6 hours at 100—150°, gives a *carbonate* which separates from alcohol in large crystals, a *picrate* which melts at 115°, and an acid *chromate*, $2C_{12}H_{15}N_3,3CrO_3$, melting at 115—116°. The *benzoyl* derivative, $C_{19}H_{19}ON_3,H_2O$, crystallises from water in lustrous prisms and melts at 146°.

5-*Methylimino*-1-*phenyl*-2 : 3 : 4-*trimethylpyrazolone* closely resembles the preceding compound; the *picrate* melts at 123° and the *methiodide* at 130°.

3-*Imino*-1-*phenyl*-2 : 5-*dimethylpyrazolone*, $NPh<\begin{matrix}CMe:CH \\ NMe\cdot C:NH\end{matrix}$, prepared from 3-chloro-1-phenyl-5-methylpyrazole 2-methochloride (*iso*-antipyrine chloride) and aqueous ammonia at 150°, gives a crystalline *carbonate* and *picrate*. W. A. D.

o-Dianisylthiodicyanodiamine. H. Klut (*Ber.*, 1903, **36**, 3322—3325).—*o*-*Dianisylthiodicyanodiamine*,

$$OMe\cdot C_6H_4\cdot NH\cdot C(NH)\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot OMe,$$

prepared by the action of sulphur dichloride or thiophosgene on a chloroform solution of *o*-anisylthiocarbamide (compare the formation of thiodicyanodiamine from thiocarbamide, Rathke, Abstr., 1879, 41), separates from a mixture of benzene and light petroleum in white leaflets, melting at 80—82°, is a monacidic base, insoluble in water but easily soluble in most organic solvents, and becomes dark yellow on exposure to light. Its *picrate* softens at 175° and melts completely at 198°. Its *monoacetyl* derivative crystallises from alcohol in rhombic leaflets and melts at 205—206°. Its *nitrite* melts at 129°, and, when warmed with water, forms the *nitroso*-derivative,

$$OMe\cdot C_6H_4\cdot N(NO)\cdot C(NH)\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot OMe,$$

which separates from alcohol in orange-coloured, prismatic needles and melts at 171—172°.

o-Dianisylthiodicyanodiamine unites with phenylcarbimide to form the *compound*, $C_{16}H_{18}O_2N_4S,PhN:CO$, which crystallises from dilute alcohol in tiny leaflets and melts at 185°. The corresponding compound with phenylthiocarbimide melts at 210—211°.

A. McK.

m-**Azoxybenzaldehyde and its Analogues.** ALFRED HUMAN and HUGO WEIL (*Ber.*, 1903, 36, 3469—3475).—*m*-Azoxybenzaldehyde has been prepared by Alway (Abstr., 1903, i, 201, 706). A 70 per cent. yield is obtained by the reduction of *m*-nitrobenzaldehyde with ferrous hydroxide. On extracting the product with a solution of sodium hydrogen sulphite and boiling with sulphuric acid, the azoxy-compound is precipitated. In its condensations, both aldehyde groups react simultaneously. The *bisphenylhydrazone*, $ON_2(C_6H_4 \cdot CH{:}N \cdot NHPh)_2$, forms yellow crystals melting at 198°, the *dioxime*,

$$ON_2(C_6H_4 \cdot CH{:}N \cdot OH)_2,$$

melts at 191°. When boiled with it, aniline reacts slowly, yielding m-*azoxybenzylideneaniline*, which forms yellow crystals melting at 125°. Hydrazine forms a yellow precipitate of the *aldazine*,

$$CH \lessgtr \begin{matrix} C_6H_4 \cdot ON_2 \cdot C_6H_4 \\ N \text{———————} N \end{matrix} \gtrless CH.$$

Dimethylaniline and sulphuric acid form m-*azoxyleucomalachite-green*, $ON_2[C_6H_4 \cdot CH(C_6H_4 \cdot NMe_2)_2]_2$, melting at 176° and yielding a yellowish-green dye on oxidation with lead peroxide.

Heating with concentrated sulphuric acid at 110° converts *m*-azoxybenzaldehyde into m-*benzaldehydeazobenzoic acid*,

$$CHO \cdot C_6H_4 \cdot N{:}N \cdot C_6H_4 \cdot CO_2H,$$

melting at 163°. The *sodium* salt is partially hydrolysed by water. The *ethyl* ester melts at 156°. Hydrazine forms the *aldazine*, melting above 330°. The *oxime* forms yellow crystals which melt at 185°. The compound with phenylhydrazinesulphonic acid was also prepared. *Benzylideneanilineazobenzoic acid*, $CO_2H \cdot C_6H_4 \cdot N{:}N \cdot C_6H_4 \cdot CH{:}NPh$, is faintly yellow coloured and melts at 128°.

p-Azoxybenzaldehyde (compare Alway, Abstr., 1902, i, 649) may be prepared in similar manner. Concentrated sulphuric acid converts it into p-*benzaldehydeazobenzoic acid*, melting above 330° and forming an *ethyl* ester melting at 60°. C. H. D.

m-**Azoxybenzaldehyde and its Analogues.** ALFRED HUMAN and HUGO WEIL (*Ber.*, 1903, 36, 3801—3802. Compare preceding abstract). —To ascertain whether the intermolecular rearrangement of *m*-azoxybenzaldehyde into benzaldehydazobenzoic acid, which takes place when it is acted on by concentrated sulphuric acid, is not due to the oxidising influence of one molecule of the azo-compound on a second, the reaction was carried out in presence of the easily oxidisable benzaldehyde; this was, however, recovered unchanged. The rearrangement is thus apparently a consequence of the oxidation of the aldehyde group of the distant nucleus, by the oxygen atom attached to nitrogen. E. F. A.

The Three Isomeric Nitronitrosobenzenes. EUGEN BAMBERGER and RUDOLF HÜBNER (*Ber.*, 1903, 36, 3803—3822).—Alway (Abstr., 1903, i, 690) has prepared *m*-nitronitrosobenzene by oxidising the solution obtained from the reduction of *m*-dinitrobenzene with zinc and acetic acid. The authors had examined this action before the publication of Alway's paper, and the results have been partly published (Hübner, *Inaug. Diss.*, Zürich, 1902).

o-*Nitronitrosobenzene*, $ON\cdot C_6H_4\cdot NO_2$, prepared by oxidising *o*-nitroaniline with Caro's acid, separates from water in almost colourless needles and melts at 126—126·5° to a green liquid. Small amounts of *o*-dinitrobenzene and *o*-*o*′-dinitroazoxybenzene were also isolated from the product of the oxidation.

m-Nitronitrosobenzene, prepared from *m*-nitroaniline and Caro's acid, separates from water in colourless, glistening needles and melts at 89·5—90·5° to a green liquid (Alway gives 85°). *m*-*m*′-Dinitroazoxybenzene, produced during the oxidation in about the same amount as *m*-nitronitrosobenzene, separates from concentrated nitric acid in yellow needles and melts at 144—145°. A trace of *m*-dinitrobenzene was also formed during the oxidation.

p-*Nitronitrosobenzene*, prepared from *p*-nitroaniline and Caro's acid, separates from alcohol in orange-coloured needles and melts at 118·5—119° to a green liquid. When oxidised, it readily yields *p*-dinitrobenzene.

p-p′-*Dinitroazoxybenzene*, melting at 222°, is also formed during the oxidation.

p-*Nitroazobenzene*, prepared by adding aniline to a solution of *p*-nitronitrosobenzene in glacial acetic acid, forms salmon-coloured leaflets or flat needles and melts at 134—135°. *m*-Nitroazobenzene was prepared in an analogous manner, and also by combination of nitrosobenzene and *m*-nitroaniline.

o-o′-*Dinitroazoxybenzene*, prepared by the action of alcoholic potash on *o*-nitronitrosobenzene, crystallises in flat, glistening needles and melts at 175—175·5°. The filtrate, from which the crude *o*-*o*′-dinitroazoxybenzene had been removed, was extracted with ether and then acidified; nitrous acid was formed, and o-*nitro*-o′-*hydroxyazoxybenzene*, crystallising in silky needles and melting at 91—92°, was precipitated. Evidence for its constitution was further adduced by its behaviour on reduction, when *o*-aminophenol and *o*-phenylenediamine were formed.

o-Nitronitrosobenzene, when boiled with water, gives *o*-nitro-*o*′-hydroxyazoxybenzene, *o*-*o*′-dinitroazoxybenzene, *o*-dinitrobenzene, *o*-nitrophenol, *o*-nitroaniline, and other products contained in a tar, which was not further examined.

o-Dinitrobenzene is easily prepared by oxidising *o*-nitronitrosobenzene.

A series of *o*-nitroazo-derivatives, prepared by the condensation of *o*-nitronitrosoaryl derivatives with aromatic amines, is described. o-*Nitroazobenzene*, $NO_2\cdot C_6H_4\cdot N_2Ph$, prepared from *o*-nitronitrosobenzene and aniline, separates from alcohol in glassy, orange-coloured prisms and melts at 70·5—71°. o-*Nitrobenzene*-o-*azotoluene*, prepared from *o*-nitronitrosobenzene and *o*-toluidine, separates from alcohol in orange-coloured needles and melts at 85°. o-*Nitrobenzene*-p-*azotoluene* separates from alcohol in silky, orange-red needles and melts at 88°. o-*Nitrobenzeneazo*-p-*chlorobenzene*, prepared from *o*-nitronitrosobenzene and *p*-chloroaniline, crystallises in orange-red leaflets with greenish-golden lustre and melts at 145—146°. o-*Nitrobenzeneazo*-2 : 4-*dichlorobenzene*, prepared from *o*-nitronitrosobenzene and 2 : 4-dichloroaniline, separates

from alcohol in salmon-coloured, silky needles and melts at 155·5°. o-*Nitrobenzeneazo*-2 : 4 : 6-*trichlorobenzene*, prepared from *o*-nitronitrosobenzene and 2 : 4 : 6-trichloroaniline, separates from alcohol in straw-coloured, glistening leaflets and melts at 143°. o-*Nitrobenzeneazo*-p-*bromobenzene*, prepared from *o*-nitronitrosobenzene and *p*-bromoaniline, forms brick-red leaflets of greenish-golden lustre and melts at 152·5°.

4-*Nitroso-3-nitrotoluene*, prepared by oxidising *m*-nitro-*p*-toluidine by Caro's acid, separates from alcohol in greenish-yellow needles and melts at 145—145·5°. By combination with aniline, it forms 2-*nitro*-p-*tolueneazobenzene*, which crystallises in glistening leaflets or needles and melts at 71—71·5°. A. McK.

Reduction of *o*-Nitroazo-compounds. Eugen Bamberger and Rudolf Hübner (*Ber.*, 1903, 36, 3822—3827. Compare preceding abstract).—Whilst nitroso-compounds, on account of the ease with which they are reduced, can be detected only with some difficulty during the reduction of nitro-compounds, the case is otherwise with *o*-nitroazo-compounds. The nitroso-derivative, presumably the initial product of the reduction of *o*-nitroazo-compounds, is not further reduced, but undergoes intramolecular rearrangement into the stable "azoimino-oxides."

When *o*-nitroazobenzene is reduced by sodium sulphide, benzeneazoiminobenzene oxide is formed, thus:

$$NO_2 \cdot C_6H_4 \cdot N_2Ph + H_2 \longrightarrow (NO \cdot C_6H_4 \cdot N_2Ph) \longrightarrow C_6H_4 < \overset{N-}{\underset{NO}{|}} > NPh.$$

The latter substance separates from light petroleum in glistening needles and melts at 88·5°. It is reduced by tin and hydrochloric acid to phenylazoiminobenzene, $C_6H_4 < \overset{N}{\underset{N}{|}} > NPh$, melting at 109·5° and identical with the compound described by Gattermann and Wichmann (Abstr., 1888, 829) as 2-phenylphenotriazole.

p-*Bromophenylazoiminobenzene oxide*, $C_6H_4 < \overset{N-}{\underset{NO}{|}} > N \cdot C_6H_4Br$, prepared by the reduction of *o*-nitrophenylazo-*p*-bromobenzene by sodium sulphide, forms white, glistening needles and melts at 162—162·5°. When reduced by stannous chloride and concentrated hydrochloric acid, it forms p-*bromophenylazoiminobenzene*, $C_6H_4 < \overset{N}{\underset{N}{|}} > N \cdot C_6H_4Br$, which separates from alcohol in silky needles and melts at 174°.

p-*Chlorophenylazoiminobenzene oxide* crystallises in needles and melts at 155·5—156·5°. On reduction by stannous chloride, it yields p-*chlorophenylazoiminobenzene*, which crystallises in needles and melts at 167·5—168·5°.

Phenylazoiminotoluene oxide, $C_6H_3Me < \overset{N-}{\underset{NO}{}} > NPh$, prepared from 2-nitro-*p*-tolueneazobenzene and sodium sulphide, crystallises in slightly yellow leaflets and melts at 142·5°. When reduced by

stannous chloride, it forms *phenylazoiminotoluene*, which separates from alcohol in glistening prisms and melts at 98·5°.

A. McK.

Oxidation of *p*-Phenylenediamine. EUGEN BAMBERGER and RUDOLF HÜBNER (*Ber.*, 1903, 36, 3827—3831. Compare preceding abstracts).—*p*-Nitroaniline is the main product of the oxidation of *p*-phenylenediamine in aqueous solution by Caro's acid. This is an instance of the ease with which the hydroxylamino-group is oxidised as compared with the amino-group, since the reaction undoubtedly proceeds thus: $C_6H_4(NH_2)_2 \rightarrow (NH_2 \cdot C_6H_4 \cdot NH \cdot OH \rightarrow NH_2 \cdot C_6H_4 \cdot NO) \rightarrow NH_2 \cdot C_6H_4 \cdot NO_2$. A comparatively small part of the *p*-nitroaniline, formed in this manner, is further oxidised with the production of *p*-dinitrobenzene and *p*-*p'*-dinitroazoxybenzene, thus:

$$NO_2 \cdot C_6H_4 \cdot NH_2 \rightarrow \underbrace{(NO_2 \cdot C_6H_4 \cdot NH \cdot OH \rightarrow NO_2 \cdot C_6H_4 \cdot NO)}_{\downarrow \atop ON_2(C_6H_4 \cdot NO_2)_2.} \rightarrow C_6H_4(NO_2)_2$$

When the oxidation of *p*-phenylenediamine by Caro's acid is conducted in ethereal solution, *p*-nitrosoaniline can be isolated as well as *p*-nitroaniline.

A. McK.

Liquid Crystals. RUDOLF SCHENCK and ERNST EICHWALD (*Ber.*, 1903, 36, 3873—3877. Compare Abstr., 1898, ii, 286, 593; 1899, ii, 360; 1900, ii, 339; Rotarski, Abstr., 1903, i, 869; ii, 137).—*p*-Azoxyanisole, even after several crystallisations from methyl alcohol, contains small amounts (1·5 per cent.) of *p*-azoanisole. The presence of this impurity is readily detected by the red colour which it develops on the addition of hydrochloric acid, and it may be completely removed by crystallising the azoxyanisole several times from a mixture of concentrated hydrochloric acid (1 part) and glacial acetic acid (3 parts). The pure product forms pale yellow prisms, melts to a cloudy liquid at 116°, and suddenly becomes clear at 135·2°. Rotarski's statement that, when free from *p*-azoanisole, the azoxy-compound melts immediately to a clear liquid is not correct.

When *p*-azoxyanisole is kept for some time at 130°, small amounts of *p*-azoanisole are formed.

J. J. S.

A New Sensitive Indicator from *m*-Toluidine. JULIUS TRÖGER and W. HILLE (*J. pr. Chem.*, 1903, [ii], 68, 297—309).—The action of sulphur dioxide on diazotised *m*-toluidine in very dilute sulphuric acid solution leads to the formation of a *sulphonic acid*, $C_{14}H_{15}N_4 \cdot SO_3H$, as a blood-red, voluminous precipitate. On adding its potassium salt to dilute hydrochloric acid, the sulphonic acid is obtained in ruby-red, prismatic needles. It decomposes at 100°, evolves sulphur dioxide when heated, is only slightly soluble in water, forming a carmine solution, and dissolves in aqueous alkali hydroxides or carbonates, or ammonia to form yellow solutions from which it is liberated by mineral acids, but not by acetic acid. As an indicator, the sulphonic acid is used in the form of its sodium salt; in its colorations and scope of application, it resembles, but is more sensitive than, helianthin.

The *potassium, sodium, barium,* and *ammonium* salts are described.

The sulphonic acid probably has the constitution

$$SO_3H{\cdot}C_7H_6{\cdot}N_2{\cdot}C_7H_5(NH_2)_2.$$

When reduced by concentrated hydrochloric acid and stannous chloride, it forms a colourless solution from which only a small amount of the hydrochloride of a base has been obtained. The action of diazotised *m*-toluidine on 2 : 4-diaminotoluene leads to the formation of a *diaminoazotoluene*, $C_7H_7{\cdot}N_2{\cdot}C_7H_5(NH_2)_2$, which crystallises from ethyl acetate, on addition of light petroleum, in small, dark cherry-red crystals. G. Y.

Diazo-ethers. HANS EULER (*Ber.*, 1903, 36, 3835—3837).—In spite of Hantzsch's communication (Abstr., 1903, i, 869), the author is still of opinion that his experiments (Abstr., 1903, i, 722) support Bamberger's view that the products of saponification of diazo-ethers are normal diazoxides. A. McK.

Aniline Bases and Nitrous Esters in Alkaline Solution. HANS EULER (*Ber.*, 1903, 36, 3837—3840. Compare preceding abstract).—It is supposed by Hantzsch that diazo-ethers decompose, under the conditions employed by Bamberger and by the author, into aniline base and nitrous ester, thus :

$$\begin{array}{l}Ar{\cdot}N\\ \quad\| \\ N{\cdot}OMe + H_2O\end{array} \longrightarrow ArNH_2 + NO{\cdot}OMe.$$

Hantzsch further holds that the coupling with β-naphthol observed by Bamberger and by the author was due to the presence of those decomposition products. The author now proves that those decomposition products do not couple with β-naphthol in alkaline solution.

Aniline was shaken with an aqueous solution of sodium hydroxide containing *iso*amyl nitrite on the one hand and methyl nitrite on the other. Those solutions, after being extracted with ether, did not couple with the β-naphthol solutions previously employed by the author (Abstr., 1903, i, 722).

Hantzsch's views in this matter are, therefore, contradictory to facts. A. McK.

Colour of Aqueous Solutions of Methyl-orange and the Change which Acids produce in it. P. VAILLANT (*Compt. rend.*, 1903, 137, 849—851).—The well known colour change produced in yellow solutions of methyl-orange by the addition of acids has been explained in two ways. Ostwald (*Grundlagen der Anal. Chimie, ch.* 6) maintains that the red tint is due to the undissociated molecule whilst the anions of the dye give rise to the yellow colour. Küster (*Zeit. physikal. Chem.*, 1897, 13, 127) also supposes the yellow colour to be due to the anion, $NMe_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}\overset{-}{SO_3}$, but assigns the red to the electrically neutral group $\overset{+}{H}{\cdot}NMe_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4\overset{-}{SO_3}$, which is formed on bringing hydrogen ions into solutions containing the yellow anion. The author shows that neither of these hypotheses are in accordance with his observations. It was found that the molecular absorption of aqueous solutions of methyl-orange remains constant at

all dilutions in spite of varying dissociation. This fact seems to prove that both the undissociated molecule and anion gave the same colour, hence the colour changes produced by acids cannot be explained by dissociation. It is also shown that the absorption coefficient of aqueous solutions undergoes a great change when acids are added, an effect which varies in intensity with the strength of the acid. The author concludes that the molecule of methyl-orange undergoes a change in structure under the influence of acids, the product being red in colour. Red crystals were obtained by evaporating an acidified alcoholic solution of the dye (compare also Stieglitz, this vol., ii, 17).

S. S.

Diazoanhydrides and 1-Amino-1 : 2 : 3-triazole. LUDWIG WOLFF and A. A. HALL (*Ber.*, 1903, **36**, 3612—3618).—The compounds formed by the condensation of diazoanhydrides with phenylhydrazine or semicarbazide (Wolff, Abstr., 1903, i, 203) are derivatives of 1-aminotriazole. The primary triazole bases cannot be prepared by means of hydrazine under the same conditions, but result from the decomposition of the 1-carbamidotriazoles by acids.

The *anhydride* of *ethyl diazobenzoylacetate*, $O<\genfrac{}{}{0pt}{}{CPh}{N:N}>C\cdot CO_2Et$, is obtained by the careful reduction of ethyl *iso*nitrosobenzoylacetate, which may be prepared by the general method for these compounds (*loc. cit.*, Perkin, Trans., 1885, **47**, 244). The diazoanhydride is a yellow oil, dissolving in ether or alcohol but insoluble in water, and having a sp. gr. 1·2138 at 0°, very stable towards cold dilute acids or iodine, but decomposed by hot acids or alkalis. Semicarbazide forms *ethyl 1-carbamido-5-phenyltriazole-4-carboxylate*,

$$NH_2\cdot CO\cdot NH\cdot N<\genfrac{}{}{0pt}{}{N:N}{CPh}>C\cdot CO_2Et,$$

which crystallises from alcohol in bundles of needles melting at 208°, and dissolves in sodium carbonate, being reprecipitated by carbon dioxide. Sodium hydroxide hydrolyses it to the *carboxylic acid*, which forms a granular mass, melting and decomposing at 208°, dissolving sparingly in ether, hot alcohol, or water.

Carbamidomethyltriazolecarboxylic acid (*loc. cit.*) is decomposed by hydrochloric acid, forming aminomethyltriazolecarboxylic acid, which is best isolated by means of its *benzylidene* compound, $C_{11}H_{10}O_2N_4$, crystallising in colourless needles and melting and decomposing at 170°. Hot acids or alkali hydroxides hydrolyse it, forming *1-amino-5-methyltriazole-4-carboxylic acid*, which crystallises from water in slender, colourless needles or prisms and decomposes at 190° into carbon dioxide and aminomethyltriazole. Solutions of the salts have no reducing action on Fehling's solution or ammoniacal silver nitrate in the cold. The acid condenses with a hot solution of acetaldehyde, forming a *compound* which crystallises in needles and melts and decomposes at 153°.

1-Benzylideneamino-5-methyltriazole, $CHPh:N\cdot N<\genfrac{}{}{0pt}{}{N:N}{CMe}>CH$, prepared by heating benzylideneaminomethyltriazolecarboxylic acid at about 200° until the evolution of carbon dioxide ceases, crystallises

from light petroleum in colourless prisms or tablets melting at 67—68°, and forms a *hydrochloride* which crystallises in needles and melts and decomposes at 135—140°. Hydrochloric acid hydrolyses the benzylidene derivative to benzaldehyde and 1-*amino-5-methyltriazole*, $NH_2\cdot N<\genfrac{}{}{0pt}{}{N:N}{CMe}>CH$, which crystallises from benzene in colourless leaflets melting at 70° and dissolves readily in water, alcohol, or chloroform, less readily in ether. The solution has a neutral reaction, and reduces gold chloride on warming, but not Fehling's solution or ammoniacal silver nitrate. The *hydrochloride*, $C_3H_6N_4,HCl$, crystallises from alcohol in colourless needles, which melt and decompose at 138°. The aqueous solution has an acid reaction and reduces Fehling's solution on heating. The *platinichloride* is yellow and granular, the *aurichloride* is oily. C. H. D.

Formation of Azo-compounds. Reduction of *o*-Nitrobenzyl Methyl Ether. PAUL FREUNDLER (*Compt. rend.*, 1903, **137**, 521—523. Compare Abstr., 1903, i, 371).—In addition to the substances already detected (*loc. cit.*) among the reduction products of *o*-nitrobenzyl alcohol, the author has recognised *o*-azobenzyl alcohol,

$$N_2(C_6H_4\cdot CH_2\cdot OH)_2,$$

which, in the process of isolation, passes into indazyl-*o*-benzyl alcohol, $C_6H_4<\genfrac{}{}{0pt}{}{N—}{CH}>N\cdot C_7H_6\cdot OH$. When *o*-nitrobenzyl methyl ether is reduced by zinc dust and sodium hydroxide in presence of alcohol, there are formed anthranilic acid, indazyl-*o*-benzoic acid (*loc. cit.*), *o*-aminobenzyl methyl ether, the *oxalate* of which melts at 124°, a yellow *resin* soluble in ether and acids, and having the properties of benzylene-imine, $\left(C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{NH}\right)_n$, and *o-azobenzyl methyl ether*,

$$N_2(CH_2\cdot C_6H_4\cdot OMe)_2,$$

which crystallises in red prisms, melts at 68·5°, and when heated at 150—200° is converted into *indazylbenzyl methyl ether* (compare Abstr., 1903, i, 585), $C_6H_4<\genfrac{}{}{0pt}{}{CH}{N—}>N\cdot C_7H_6\cdot OMe$. The formation of these substances indicates that the ether is first partially saponified by the sodium hydroxide. *o*-Nitrobenzyl ethyl ether furnishes similar products on reduction by this method. T. A. H.

Reduction Products of Azo-compounds. X. Reduction of Toluene-*o*-azophenetole and Bromobenzeneazophenetoles with Acid Reducing Agents. PAUL JACOBSON, GEORG FRANZ, and KARL ZAAR (*Ber.*, 1903, **36**, 3857—3872. Compare Abstr., 1896, i, 23, 24, 27, 96; 1898, i, 440).—The products obtained by the reduction of toluene-*o*-azophenetole with tin chloride and hydrochloric acid have been reinvestigated, and it is now found that some 20 per cent. of an *o*-semidine is formed and may be separated by the formic acid method. The yield of *o*-semidine is better when Witt and Helmont's method (Abstr., 1894, i, 606) of reduction is adopted. The three bromobenzeneazophenetoles have also been reduced and they behave very similarly to the corresponding methyl compound. A table is given

showing the amount of *o*- and *p*-semidines and decomposition products obtained from various substituted benzeneazophenetoles. A substituent in the positions 2 or 2′ tends to diminish the amount of *o*-semidine and to increase the amount of *p*-semidine, although the influence is not so marked as first stated. A substituent in the position 3′ also appears to diminish the amount of *o*-semidine and it appears questionable whether the lessening of *o*-semidine formation is to be attributed to steric influences.

2-*Amino*-5-*ethoxy*-2′-*methyldiphenylamine*, obtained from toluene-*o*-azophenetole by Witt and Helmont's process, crystallises from light petroleum in colourless plates melting at 82—83°. It reacts with nitrous acid and gives the characteristic azimide formation. Boiling with formic acid converts the base into 6-*ethoxy*-1-*o*-*tolylbenziminazole*, $OEt\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{N}{N(C_6H_4Me)}{>}CH$, which crystallises in needles melting at 77—78°. The *stilbazonium* base, $OEt\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{N{=\!=}CPh}{N(C_6H_4Me)}{>}CPh\cdot OH$ (compare Kehrmann and Woulfson, Abstr., 1899, i, 506; Hantzsch and Kalb, 1900, i, 114), crystallises in yellow plates melting at 172°.

The *diformyl* derivative of the *p*-semidine,

$$OEt\cdot C_6H_4\cdot N(CHO)\cdot C_6H_3Me\cdot NH\cdot CHO$$

[OEt : Me : NH = 4 : 3′ : 4′], crystallises from dilute alcohol in prisms melting at 140°.

In the preparation of *o*-bromobenzeneazophenol (Hewitt, Moore and Pitt, Abstr., 1898, i, 653), a hydroxybenzenebisazo-*o*-bromobenzene, $(C_6H_4Br\cdot N_2)_2\cdot C_6H_3\cdot OH$, is formed. It crystallises in reddish-brown plates, melts at 160°, and is readily soluble in benzene or acetic acid. o-*Bromobenzeneazophenetole* crystallises from alcohol in yellowish-red plates, melts at 39°, and is readily soluble in most solvents. When reduced by Witt's process it yields a *p*-semidine, 3-*bromo*-4-*amino*-4′-*ethoxydiphenylamine*, $OEt\cdot C_6H_4\cdot NH\cdot C_6H_3Br\cdot NH_2$, in the form of colourless plates melting at 54°. The *hydrochloride* and *sulphate* are both sparingly soluble, and the m-*nitrobenzylidene* derivative melts at 137—138°. An *o*-semidine is also formed during the reduction and may be isolated in the form of its methylene compound, 6-*ethoxy*-1-o-*bromophenylbenziminazole*, the picrate of which melts at 176°.

m-Bromobenzeneazophenol melts at 139—140° (Hewitt, 136°) and the *ethyl* ether at 68°. *Hydroxyphenylbisazo*-m-*bromobenzene* crystallises in needles and melts at 162—163°. 3′-*Bromo*-2-*amino*-5-*ethoxydiphenylamine* yields a crystalline *hydrochloride*, condenses with benzil to form 2-*hydroxy*-7-*ethoxy*-1-m-*bromophenyl*-2 : 3-*diphenyl*-1 : 2-*dihydroquinoxaline*, $OEt\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{N{=\!=}CPh}{N\cdot(C_6H_4Br)}{>}CPh\cdot OH$, in the form of yellow crystals melting at 166—169°. With carbon disulphide, it yields 2-*thiol*-6-*ethoxy*-1-m-*bromophenylbenziminazole*,

$$OEt\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{N}{N(C_6H_4Br)}{>}C\cdot SH,$$

which crystallises in colourless needles melting at 201°.

6-*Ethoxy*-1-m-*bromophenylbenziminazole*, $OEt\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{N}{N(C_6H_4Br)}{>}CH$, crystallises in colourless needles and melts at 130°; the *picrate* forms

yellow needles and melts at 220—221°. The *o*-semidine yields an *o-hydroxybenzylidene* derivative,

$$OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_3(OEt)\cdot NH\cdot C_6H_4Br,$$

melting at 116°. J. J. S.

Azo-compounds from Aziminonaphthalenesulphonic Acids. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 139908 and 143387).—Azo-dyes prepared from diazotised *o*-aminophenols and 1 : 8 diaminonaphthalene-4-sulphonic acid react with hydrochloric acid and sodium nitrite, forming azo-compounds of 1 : 8-aziminonaphthalene-4-sulphonic acid. *p*-Nitro-*o*-aminophenol, picramic acid, and 6-nitro-2-aminophenol-4-sulphonic acid yield suitable diazonium compounds. The same dyes may also be prepared by the direct combination of the diazonium compounds with 1 : 8-aziminonaphthalene-4-sulphonic acid. C. H. D.

Solid Azo-dyes derived from 1-Aminoanthraquinone. Charles Lauth (*Compt. rend.*, 1903, 137, 661—664).—1-Diazoanthraquinone combines readily with amines and phenols and their sulphonic acid derivatives to form solid, soluble dyes, rich in colour; those derived from the naphtholsulphonic acids and aminonaphtholsulphonic acids are not affected by light, and resist the process of fulling. Anthraquinoneazo-β-naphthol-8-sulphonic acid is a *red* dye, which can be employed in the presence of chromic acid to obtain mixed dyes; similar dyes are afforded by β-naphthol-6-sulphonic acid, β-naphthol-3 : 7-disulphonic acid, β-naphthol-3 : 8-disulphonic acid, β-naphthol-7-sulphonic acid, and naphthionic acid.

Amaranth dyes are afforded by Piria's salt (α-naphtholsulphonic acid) and "chromotrope" acid (1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid); *violet* dyes by α-naphthylamine and 8-amino-α-naphthol-3 : 6-disulphonic acid; and *brown* dyes by α-naphthol, resorcinol, *m*-aminophenol, *o*- and *m*-cresotic acids, β-naphthylamine-6-sulphonic acid (Brönner's salt), tolylenediamine, β-naphthylamine, diphenylamine, and salicylic acid.

The sulphonic acid derivatives of 1-diazoanthraquinone give similar series of azo-dyes, which are more soluble in water than those already described. M. A. W.

Mixed Tetrazo-compounds. Eugen Bamberger and Johannes Frei (*Ber.*, 1903, 36, 3833—3835).—It is known that nitroparaffins, like phenols, interact with diazonium salts to form hydrazones. Diazotised *s*-trichloroaniline acts on nitroethane to form a mixture of nitroacetaldehydetrichlorophenylhydrazone and the mixed tetrazo-compound, bistrichlorophenylazonitroethane, thus:

(1) $CH_2Me\cdot NO_2 + C_6H_2Cl_3\cdot N_2\cdot OH = NO_2\cdot CMe\colon N_2H\cdot C_6H_2Cl_3 + H_2O$

and

(2) $CH_2Me\cdot NO_2 + 2C_6H_2Cl_3\cdot N_2\cdot OH = NO_2\cdot CMe(N_2\cdot C_6H_2Cl_3)_2 + 2H_2O$.

The mixture is separated by sodium hydroxide, in which the tetrazo-compound is insoluble.

Bis-2 : 2 : 4-*trichlorophenylazonitroethane* separates from acetone in tiny needles and melts at 97·5°.

Bis-2 : 2 : 4-*tribromophenylazonitroethane*, prepared from nitroethane

and tribromodiazobenzene, forms ochre-coloured crystals which melt and decompose at 98°.

Nitroacetaldehyde-2 : 2 : 4-tribromophenylhydrazone separates from alcohol in golden-yellow, glistening leaflets and melts at 116—117°.

A. McK.

1-Phenyl-3-methylpyrazole-4-azobenzene. AUGUST MICHAELIS and R. LEONHARDT (*Ber.*, 1903, 36, 3597—3599).—*5-Chloro-1-phenyl-3-methylpyrazole-4-azobenzene*, $N\Big\langle{NPh\cdot CCl \atop CMe\cdot \overset{||}{C}\cdot N{:}NPh}$, prepared by heating phenylmethylpyrazolone-azobenzene with phosphorus oxychloride at 120°, crystallises from hot alcohol in slender, yellow needles, melts at 190°, and has feeble basic properties, but does not combine with methyl iodide; the chlorine is not eliminated by aqueous or alcoholic potash, but the compound can be readily reduced in alkaline solution.

1-Phenyl-3-methylpyrazole-4-azobenzene, $N\Big\langle{NPh\cdot CH \atop CMe\cdot \overset{||}{C}\cdot N{:}NPh}$, prepared by the action of zinc dust and sodium hydroxide on the preceding compound, crystallises from alcohol in small, reddish-yellow flakes, melts at 126°, and is isomeric with the compound described by Beyer and Claisen (Abstr., 1888, 827); it crystallises unchanged from hydrochloric acid, is insoluble in alkalis, and appears to be reduced to the colourless hydrazo-compound by tin and hydrochloric acid.

T. M. L.

Precipitation of Colloids. KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1903, 4, 300—322. Compare Pauli, Abstr., 1902, ii, 388; 1903, i, 299).—There is no radical difference between the precipitation of colloids and proteids by neutral salts or by alcohols. The action of various salts is quite different and depends both on the metallic and acid radicle present, and also on the nature of the colloidal substance. The concentration of the solution is also an important factor, as more highly concentrated solutions are more readily precipitated than dilute ones.

The process of "salting out" is not merely a withdrawal of the solvent depending on the amount of the precipitating agent employed. In the typical case of "salting out" of a proteid, two layers are always formed, each of which contains the three substances, proteid, salt, water, but with different concentrations. The upper layer contains much water and salt, and only a little proteid, the lower contains much proteid and only little salt and water. For different temperatures, the ratio of water to salt in the precipitated layer may be the same, but the ratio of salt to proteid is not, and hence the precipitate is not a compound of the proteid and salt.

With solutions of gelatin, it has been found that the higher the concentration of the salt solution the less water does the gelatin layer contain and, on the other hand, the aqueous layer becomes poorer in gelatin. The method of salting is therefore a workable method for separating proteids and gives quantitative results, which are better than those obtained by such processes as that of ether extraction.

The partition coefficient does not merely depend on the solubility,

but also on a factor termed the "solubility intensity" (the intensity with which, for example, salt and water combine is greater than that of proteid and water). The solution pressure is thus not merely influenced by the osmotic pressure, but also by the solubility intensity.

The temperature of coagulation of albumin solutions is reduced by the introduction of monohydric alcohols of the fatty series, and the greater the amount of alcohol present the lower is the temperature. The lower homologues are not so effective as the higher alcohols.

Polyhydric alcohols (glycerol, mannitol, &c.) retard coagulation and render the coagulation less complete. Phenols produce precipitation, but even with excess of phenol, this is not complete. With resorcinol, the precipitation does not occur so readily, and on the addition of 45 per cent. of the phenol the original precipitate redissolves.

A solution of potassium acetate completely inhibits precipitation of albumin. Other salts, for example, calcium, magnesium, zinc, and mercuric chlorides, mercuric acetate, and potassium thiocyanate dissolved in methyl, ethyl, or *iso*propyl alcohol have the same effect.

Methyl and ethyl alcohols are not capable of precipitating colloidal ferric oxide, but propyl alcohol is, as is also amyl alcohol when its concentration is increased by the addition of methyl alcohol. For aqueous calcium chloride and ferric oxide solutions, the lower limit of precipitation (that is, the amount of calcium chloride required to produce opalescence) is constant if the concentration remains constant, but increases with an addition of water. The addition of methyl alcohol to the oxide solution increases the absolute amount of calcium chloride required, but the precipitation limit remains the same. J. J. S.

Tryptophan Reaction of Various Proteids. THOMAS B. OSBORNE and ISAAC F. HARRIS (*J. Amer. Chem. Soc.*, 1903, **25**, 853—855. Compare Abstr., 1903, i, 872).—The results are given of the application of the Hopkins-Cole reagent (Abstr., 1901, i, 310) to a number of vegetable proteids. In most instances, a positive reaction was obtained, but in the case of zein from maize only a very slight, transitory coloration was produced. The alcohol-soluble proteids of the oat and barley malt yielded a brown coloration which rendered the test inconclusive. The marked difference in the intensity of the reaction with different proteids indicates that the proportion of tryptophan yielded by the several proteids differs considerably. E. G.

Sulphur in Gelatin. OTTO KRUMMACHER (*Zeit. Biol.*, 1903, **45**, 310—323).—In commercial gelatin, the total percentage of sulphur found was 0·62; in purified material, 0·28. The percentage of sulphur as sulphate and sulphite respectively in commercial gelatin was 0·36 and 0·04; in pure gelatin, 0·01 and 0·01 (?). Examples are given of the method of estimating sulphur by the use of Mahler's calorimetric bomb. W. D. H.

Animal Glutins. I. Sinew Glutin. WL. S. SADIKOFF (*Zeit. physiol. Chem.*, 1903, **39**, 396—410).—A glutin has been obtained from sinews of cattle by three methods, namely, (*a*) by Van Name's

method, in which proteid impurities are fermented by the aid of trypsin; (*b*) by the repeated action of 0·25 per cent. potassium hydroxide solution; (*c*) by treatment for a short time with 0·25 per cent. potassium hydroxide, and, after washing with water, with 0·25 per cent. sodium carbonate solution.

The mean results of various analyses are: C, 50·90; H, 6·80; N, 18·2 (Kjeldahl's method) or 18·59 (Dumas' method); S, 0·34 to 0·5. These numbers agree very well with those obtained by Paal (Abstr., 1892, 895) and by Sadikoff for gelatin.

The glutin obtained by the first method exists in a form (*A*) which is sparingly soluble in cold water, but which dissolves readily in warm water and readily gelatinises, and also in a form (*B*) which is readily soluble in cold water, but the solution so obtained does not readily gelatinise. Somewhat similar modified forms have been obtained by the second method, but the differences are not shown in the results of analysis. J. J. S.

Animal Glutins. II. Cartilage-glutins (Gluteins). Wl. S. Sadikoff (*Zeit. physiol. Chem.*, 1903, 39, 411—422. Compare Mörner, Abstr., 1889, 736).—Cartilage-glutin from the pig's nasal membrane, from cattle, and from the elastic tissue from the muscle of the pig's ears, has been prepared and analysed. All specimens contain less carbon and nitrogen and more sulphur than sinew glutin. Low results are obtained for nitrogen when determined by the Kjeldahl method. After hydrolysis with acids, the glutins have only a feeble reducing action on alkaline cupric oxide solutions. They all give a reaction with hydrochloric acid and phloroglucinol in the presence of alcohol. In these respects, they differ from sinew glutin and from commercial gelatin.

Treatment of the cartilage for a short time with dilute hydrochloric acid (0·2 per cent.) renders it soluble in water and alters the composition, the carbon and hydrogen becoming higher and the nitrogen lower. J. J. S.

Plastein of Egg-albumin. D. Kuraéeff (*Beitr. chem. Physiol. Path.*, 1903, 4, 476—485. Compare Abstr., 1902, i, 731).—Plastein was obtained by the digestion of crystalline egg-albumin with gastric juice and subsequent addition of rennet to the albumose solution so obtained. Elementary analyses of two preparations are given. A change of the plastein-albumoses into coagulable proteid by the gastric mucous membrane is probable, but the results are not very conclusive.

W. D. H.

Preparation and Analysis of Nucleic Acids. VI. Phoebus A. Levene (*Zeit. physiol. Chem.*, 1903, 39, 479—483. Compare Abstr., 1901, i, 299, 300, 623; 1903, i, 668, 779; ii, 438).—A nucleic acid has been obtained from the testicles of oxen by the usual methods. It did not give the biuret and Millon's reactions, and did not reduce Fehling's solution after having been warmed for a short time with mineral acids. On hydrolysis with 1 per cent. sulphuric acid at 125°,

it gave guanine and adenine, and with 25 per cent. sulphuric acid at 150—175° thymine and cytosine.

A similar nucleic acid has been obtained from the brains of oxen. On hydrolysis with sulphuric acid, it gives the purine and pyrimidine bases already mentioned. J. J. S.

Oxidation of Thymonucleic Acid with Calcium Permanganate. Friedrich Kutscher and John Seemann (*Ber.*, 1903, **36**, 3023).—When thymonucleic acid is oxidised with calcium permanganate in feebly alkaline solution, it yields carbamide and guanidine, but not uric acid; the amount of guanidine produced corresponds with the presence in the original material of 5 per cent. of guanine. T. M. L.

Thymonucleic Acid. S. Kostytschew (*Zeit. physiol. Chem.*, 1903, **39**, 545—560).—Neumann's *a*- and *b*-nucleic acids (Abstr., 1899, i, 467; 1900, i, 319) are not pure compounds, but are mixtures in different proportions of two acids called α- and β-nucleic acids by the author. For the preparation of the pure α-acid, Neumann's *a*-acid is transformed into its barium salt, and this is treated with excess of barium acetate when a gelatinous precipitate is obtained. The solution and precipitation are repeated 3 times and the pure barium salt is then dissolved in warm water, cooled to 40°, and precipitated with methyl alcohol. This operation is repeated a second time, and the product then thoroughly washed with methyl alcohol and ether. The *barium* salt has the composition $C_{41}H_{70}O_{26}N_{14}P_4Ba_2$, and the free α-acid, $(C_{41}H_{74}O_{26}N_{14}P_4)_n$. Solutions of the sodium and barium salts are readily gelatinised, or yield gelatinous precipitates on the addition of a number of solutions of different metallic salts. The addition of alkalis or acids, or boiling for a short time, dissolves the gelatinous material. The β-acid, obtained from Neumann's *b*-acid by removal of the α-acid as its barium salt, yields salts which do not gelatinise. The barium salt has the composition

$$C_{90}H_{141}O_{61}N_{27}P_{10}Ba_6,$$

and the free acid, $C_{90}H_{153}O_{61}N_{27}P_{10}$. The β-acid, when hydrolysed with sulphuric acid and mercuric sulphate, yields about one-third as much nuclein bases as can be obtained from the same weight of the α-acid. J. J. S.

Chemical Investigations on Lymphatic Organs. II. Constitution of Natural Histon Nucleate. Ivor Bang (*Beitr. chem. Physiol. Path.*, 1903, **4**, 331—361. Compare Abstr., 1899, i, 836; 1901, i, 57, 299; 1902, ii, 36; 1903, ii, 664, 739).—When a solution of histon nucleate (nucleohiston) is saturated with sodium chloride, a precipitate of histon is obtained; the addition of alcohol to the filtrate precipitates the nucleic acid, but the clear solution still gives the biuret reaction. This is due to the presence of parahiston (Fleroff, Abstr., 1900, i, 71) in the filtrate.

According to the author, Malengreau's A- and B-histons are essentially the same compound; the reason that they give somewhat different reactions is attributed to the presence of small amounts of impurities.

Recent researches have proved that, of the five reactions described (Abstr., 1899, i, 836) as characteristic of histons, only the fourth and fifth apply generally. The histons are now placed in a special group with the protamines on account of the similarity in the properties.

Solutions of the alkali salts of the nucleic acid are not precipitated on the addition of saturated sodium chloride solution, but the addition of a few drops of acetic acid causes the immediate precipitation of the whole of the nucleic acid in the form of an acid salt.

The composition of the normal sodium salt is practically the same as that of salmonucleic acid, namely, $C_{40}H_{52}O_{26}N_{14}P_4Na_4$. When hydrolysed with 5 per cent. sulphuric acid, it yields xanthine, hypoxanthine, guanine, adenine, thymine, cytosine, lævulic acid, and formic acid, but not glycuronic acid. On distillation with magnesia, ammonia is not formed.

The acid presumably consists of two distinct nucleic acids, normal nucleic acid ($\frac{2}{3}$), and adenylic acid ($\frac{1}{3}$). Experiments lead to the conclusion that the original histon nucleate is made up of histon combined with the normal acid and parahiston combined with the adenylic acid. The two salts probably form a double compound as the original substance does not vary in composition. The formula $C_{765}H_{1188}O_{342}N_{252}S_3P_{36}$ for the double compound is suggested. The molecular weight of histon is calculated as 6122, and that of parahiston as 3060. The author's view is that the histon nucleate exists preformed in the thymus cell, but probably as part of a much larger molecule.

Histon itself forms a neutral and an acid chloride; the former precipitates proteids, but the latter does not. Histon nucleate also has acidic properties and forms alkali salts, and is capable of combining with proteids. The solubility of histon salts tends to decrease as the basicity of the acid with which the histon is combined increases.

Some 31 per cent. of the total phosphorus present in thymus cells exists in the form of histon nucleate. The nucleate has no coagulating properties. J. J. S.

Ovimucoid and Serum-mucoid. II. Carlo U. Zanetti (*Gazzetta*, 1903, 33, i, 160—164. Compare Abstr., 1899, i, 180).—Like ovimucoid (*loc. cit.*), serum-mucoid, prepared from the serum of ox-blood, yields glucosamine on hydrolysis with hydrochloric acid.

T. H. P.

Adrenalin. Hermann Pauly (*Ber.*, 1903, 36, 2944—2949. Compare Takamine, Abstr., 1902, ii, 217; 1903, i, 376; Aldrich, Abstr., 1901, ii, 564; Abel, Abstr., 1903 i, 376; von Fürth, *ibid.*, i, 669).—The analyses of adrenalin agree best with Aldrich's formula, $C_9H_{13}O_3N$. It is optically active, and has $[\alpha]_D$ $-43°$ at 23·5°. It is considered highly improbable that adrenalin contains a C:N group in the side chain, but rather that it is a secondary base containing the grouping $OH\cdot\underset{|}{C}H\cdot CH_2\cdot NHMe$ or $OH\cdot CH_2\cdot\underset{|}{C}H\cdot NHMe$. J. J. S.

Influence of Electrolytes on Enzymes. II. On Invertin. Sydney W. Cole (*J. Physiol.*, 1903, 30, 281—289).—The results

obtained justify the conclusion that electrolytes exert their effect by an influence on the ferment itself and not on the substrate, for it is in the highest degree improbable that starch and cane-sugar would respond in the same way to the addition of electrolytes.

W. D. H.

Action of Alcohol and Acids on Enzymes. THOMAS BOKORNY (*Milch.-Zeit.*, 1903, 32, 641—642).—The results of a number of experiments on the sensitiveness of enzymes towards alcohol and acids are given. Zymase is destroyed by absolute alcohol within a few minutes, and is, after a time, affected by even a 10 per cent. solution of alcohol. On the other hand, invertase still retains its inverting action after being treated for 20 days with absolute alcohol. Maltase is remarkably sensitive, its action being inhibited by dilute alcohol. Lactase is not affected by 10 per cent. alcohol,

The presence of 0·1 per cent. of sulphuric acid destroyed the action of zymase, when allowed to act on it for 5 days. 0·02 per cent. of the same acid at the ordinary temperature also had an injurious action, and destroyed the enzyme at 40°. 0·5 per cent. of lactic acid practically stopped the fermenting action of yeast within 4 days, but had no influence on lactase (compare Abstr., 1903, ii, 324).

W. P. S.

Proteolytic Enzymes. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1903, 39, 305—312).—Proteolytic enzymes (pepsin, trypsin, papain) increase the viscosity of concentrated solutions of proteolytic products. This is inhibited by the addition of the juice expressed from *Ascaris*; although the action does not occur if the juice has been previously boiled. The increase of viscosity is believed to be due to the reversed action of the enzymes, and is analogous to the plastein formation noted by others. The action of rennet is not inhibited by *Ascaris* juice.

W. D. H.

Action of Oxidising Enzymes on Carbohydrates. NADINE SIEBER (*Zeit. physiol. Chem.*, 1903, 39, 484—512).—Three oxidising enzymes (oxydases) have been obtained from the plasmafibrin of horses' blood and from other animals. Of the three enzymes, one is soluble in water, another soluble in neutral saline solution, and the third readily soluble in water and alcohol.

The normal blood plasma of horses or the plasma from horses inoculated against bubonic plague contain little or no oxydase soluble in water. It is most readily obtained from animals inoculated against diphtheria, streptococci, and staphylococci. The oxydase may be precipitated from its aqueous solution by the aid of carbon dioxide or ammonium sulphate. Its aqueous emulsion reacts with guaiacol and other reagents for detecting oxidising substances; it further gives most of the reactions characteristic of proteids. Its oxidising power begins to diminish after heating for 5 minutes at 70°. All three enzymes may be kept for some time in the dark and in the presence of thymol.

To obtain the second oxydase, the fibrin, after treatment with distilled water, is extracted with an 8 per cent. potassium nitrate solution in a thermostat. It can be precipitated by the addition of carbon dioxide, alcohol, or ammonium sulphate and purified by dialysis. It has been obtained from the fibrin of all blood sera examined and gives reactions similar to those obtained with the oxydase soluble in water, except that it gives no coloration with tincture of guaiacum in presence of hydrogen peroxide. Heating at 65° for 5 minutes tends to destroy its oxidising properties. The third oxydase, which can only oxidise in the presence of hydrogen peroxide, may be obtained from the mother liquors of the second oxydase. These are concentrated at temperatures not above 37° and all ammonium sulphate removed by the addition of alcohol. Its solution may be heated at 90° for some minutes without impairing the oxidising power to any considerable extent.

All three oxydases are capable of decomposing aqueous solutions of dextrose. After 3 days, from 80—90 per cent. of the carbohydrate has disappeared and carbon dioxide has been formed. It is also found that part of the oxygen in the air above the solution is used up, although in the case of the oxydase soluble in water the amount is but small.

When the solution of the first oxydase is heated to 100°, its activity is not completely destroyed. The three enzymes do not react so readily with solutions of sucrose, and they vary as regards their relative activities, the oxydase soluble in neutral salts yielding the largest amount of carbon dioxide and further yielding dextrose (confirmed by the formation of osazone).

The oxydase soluble in water is the most active as regards the decomposition of starch.

Oxydases from vegetable sources are also capable of inducing similar decompositions. J. J. S.

Formation of Hydrogen Sulphide by Organic Extracts and Proteids. M. Emmanuel Pozzi-Escot (*Compt. rend.*, 1903, **137**, 495—496).—When powdered sulphur or sodium hydrogen sulphite is added to an aqueous extract of yeast preserved with chloroform or sodium fluoride, hydrogen sulphide is evolved. This action does not occur unless sulphur or a sulphite is added, and is inhibited by previously boiling the extract; it must therefore be due to the activity of a reductase present in the yeast. T. A. H.

Action of Aniline Dyes on Invertin. S. S. Mereshkowsky (*Centr. Bakt. Par.*, 1903, 11, 33—45).—The action of magenta, Congo-red, and safranine respectively on invertin has been examined. A small amount of magenta does not affect the action of invertin on sucrose, whilst a larger amount entirely prevents the inversion of the sugar. Congo-red, in the proportion of one part to 1000 of solution, has no effect on invertin. The fermenting action of yeast is impaired by the presence of magenta.

Apparently invertin is not destroyed in the presence of solutions of the dyes below a certain concentration, but it forms an unstable compound with the dye. The addition of fresh sugar solution then

destroys this compound and liberates a part at least, if not the whole, of the invertin. A. McK.

Influence of Electrolytes on Amylolytic Ferments. SYDNEY W. COLE (*J. Physiol.*, 1903, 30, 202—220).—The action of dialysed ptyalin on dialysed starch is increased by the addition of very small amounts of acids and of neutral salts of strong monobasic acids. The action is decreased by the addition of large amounts of acid (0·0007 to 0·0012 per cent. of hydrochloric), and by neutral salts of weak monobasic, dibasic, and tribasic acids. The explanation advanced is that the presence of anions other than those of hydroxyl accelerates, and the presence of cathions and hydroxyl ions depresses, the activity of the enzyme. In adding an acid, there are thus two factors introduced, and the effect of various strengths of acid depends on the preponderating influence of one or the other. W. D. H.

Lipase. MAURICE DOYEN (*Compt. rend. Soc. Biol.*, 1903, 55, 1209—1211).—Polemical against Hanriot. W. D. H.

Action of Fluorescent Substances on Ferments and Toxins. HERMANN VON TAPPEINER (*Ber.*, 1903, 36, 3035—3038).—The poisonous action of fluorescent substances on infusoria is enormously intensified by the influence of light (Tappeiner and Raab, *Münch. med. Woch.*, 1900, 1). The effect of fluorescent substances on enzymes and toxins has accordingly been studied.

The conversion of starch into maltose by means of diastase is considerably retarded when eosin is present and when the solution is exposed to ordinary daylight. In the dark, eosin does not retard the formation of maltose, nor was the observed retarding effect due to the action of daylight alone. Magdala-red behaves like eosin, whilst the effect of quinoline-red is fainter than that of either eosin or Magdala-red. Acridine, dimethylphosphine, uranin, gallein, resorcinol-blue and æsculin have no action. Apparently only those fluorescent substances act, the light absorption of which lies in the green or light blue part of the spectrum. The effect is quite marked even when eosin, in the proportion of 1 : 400,000, is used.

The behaviour with invertin was analogous to that with diastase; with papayotin, a faint action was obtained by uranin and a very faint action by dimethylphosphine, whilst eosin, Magdala-red, and quinoline-red acted as with diastase and invertin.

When a solution containing ricin and a little eosin is exposed for 14 hours to diffused daylight, the ricin loses its characteristic property of coagulating red blood corpuscles; a solution containing ricin, in the absence of eosin, was unaltered in diffused daylight, whilst a solution containing both ricin and eosin was unaltered in the dark. By experiments on guinea-pigs, it was proved that the poisonous effect of a solution containing both eosin and ricin, which had been exposed to light, was less than that of a similar solution which had been kept in the dark. Uranin behaves similarly to eosin, but the action of Magdala-red, quinoline-red, and harmalin is somewhat fainter; the feeblest effect is that produced by dimethylphosphine. A. McK.

[Mercuric Derivatives of Sodium β-Naphtholsulphonates.] Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 143448 and 143726).—When sodium carbonate is added to a solution of sodium β-naphthol-6-sulphonate and mercuric chloride, a precipitate of the *compound*, $NaSO_3 \cdot C_{10}H_6O \cdot HgCl$, is obtained, separating from hot water as a colourless powder.

When sodium carbonate is added to a solution of sodium β-naphthol-3 : 6-disulphonate, and mercuric chloride is then added in the form of powder or concentrated solution, the clear solution obtained gradually deposits crystals of a *mercuric* compound, containing 32 per cent. of mercury.

The aqueous solutions of these compounds do not exhibit the characteristic reactions of the mercuric ion. C. H. D.

Silicon Compounds. III. Walther Dilthey (*Ber.*, 1903, 36, 3207—3213. Compare Abstr., 1903, i, 405, 591).—*Tri-dibenzoylmethylsilicon chloride hydrochloride*, $Si(CHBz_2)_3Cl,HCl$, forms yellow needles, which lose hydrogen chloride on exposure to air, forming the compound $Si(CHBz_2)_3Cl$, already described. The solution in pyridine or sodium carbonate is colourless, unlike that of the acetylacetonyl and benzoylacetonyl compounds, but a yellow colour is obtained on adding alcoholic potassium hydroxide to a solution of the chloride in absolute alcohol.

Dibenzoylmethane reacts with silicon bromide in chloroform solution, forming the *bromide-hydrobromide*, $Si(CHBz_2)_3Br,HBr$, which crystallises in brown needles, insoluble in ether or benzene, but dissolving in glacial acetic acid with loss of $\frac{1}{2}HBr$. On prolonged boiling with acetic acid it yields the *bromide*, $Si(CHBz_2)_3Br$, which forms opalescent plates resembling the chloride. Bromine forms the *compound*, $Si(CBrBz_2)_3Br,\frac{1}{2}HBr$, which crystallises in yellow needles, and is also obtained from bromodibenzoylmethane and silicon bromide. The *iodide*, $Si(CHBz_2)_3I$, is prepared by passing hydrogen iodide into a solution of the chloride in acetic acid, and forms stable, brownish-yellow leaflets, insoluble in ether or benzene, dissolving readily in chloroform or hot glacial acetic acid. Iodine forms brown leaflets of the *periodide*, $Si(CHBz_2)_3I_3$, which is insoluble in hot glacial acetic acid. Chloroform removes the added iodine. Picric acid reacts with the chloride in boiling chloroform solution, forming the picrate, $Si(CHBz_2)_3 \cdot C_6H_2O_7N_2$, crystallising from chloroform on addition of acetic acid and ether in yellow needles melting at 252—253°. The *hydrogen sulphate*, $Si(CHBz_2)_3 \cdot HSO_4$, crystallises from acetic acid-ether in thick, yellow prisms melting at 242°. The *nitrate* forms yellow prisms melting at 215°. With an excess of silver nitrate, the *double* salt, $2Si(CHBz_2) \cdot NO_3,AgNO_3$, is formed, crystallising in silvery needles, decomposing at 180—181°, and blackening on exposure to light. C. H. D.

Organic Chemistry.

Action of Organo-magnesium Compounds on Acetylcarbinol and its Esters. André Kling (*Bull. Soc. chim.*, 1904, [iii], 31, 16—19).—Acetylcarbinyl acetate (1 mol.) and magnesium ethyl bromide (1 mol.) react in presence of anhydrous ether to give methyldiethylcarbinol and the monoacetin of β-methylbutylene αβ-glycol.

Acetylcarbinyl benzoate (1 mol.) and magnesium ethyl bromide (4 mols.) give phenyldiethylcarbinol, magnesium benzoate and β-methylbutylene αβ-glycol, which boils at 188—189° under 760 mm. pressure.

Acetylcarbinol (1 mol.) and magnesium ethyl bromide (2 mols.) give β-methylbutylene αβ-glycol. These facts show that the esters of acetylcarbinyl behave as ketones; anhydrous acetylcarbinol reacts as a ketone, and would therefore seem to have a different constitution from that contained in solution. S. S.

Transformation of Primary α-Glycols into the Corresponding Aldehydes. Marc Tiffeneau (*Compt. rend.*, 1903, **137**, 1260—1262).—The conversion of α-primary glycols into the corresponding aldehydes by the action of sulphuric acid, first observed by Zincke in the case of α-phenylethane-αβ-diol, is a general reaction for primary substituted glycols. β-Phenylpropane-αβ-diol, melting at 38°, and β-*p*-tolylpropane-αβ-diol, melting at 36°, prepared by the action of magnesium methyl iodide on benzoylcarbinol and *p*-toluoylcarbinol respectively (compare Abstr., 1902, i, 433, and Kling, this vol., i, 2), lose a molecule of water on being heated with sulphuric acid (1 : 4), and are transformed into the corresponding aldehydes; β-phenylpropane-αβ-diol yielding hydratropaldehyde, boiling at 204°, and forming a semicarbazide melting at 156—157° (compare Abstr., 1902, i, 666), and β-*p*-tolylpropane-αβ-diol giving *p*-methylhydratropaldehyde, boiling at 219—221°, and forming a semicarbazide melting at 152°.

Since the glycol is converted into the aldehyde without change of structure, the author assumes that an intermediate vinyl alcohol is formed, which by the migration of a hydrogen atom passes into the aldehyde, thus:

$$OH{\cdot}CRMe{\cdot}CH_2{\cdot}OH - H_2O \longrightarrow CRMe{:}CH{\cdot}OH \longrightarrow CHRMe{\cdot}CHO.$$

M. A. W.

Esterification of Phosphoric Acid by Glycerol. Paul Carré (*Compt. rend.*, 1903, **137**, 1070—1073).—Phosphoric acid reacts with glycerol under the ordinary and also under reduced pressure to form three esters, containing respectively one, two, and three glyceryl residues; the first is monobasic towards helianthein and dibasic towards phenolphthalein, the second is monobasic towards both indicators, whilst the third is neutral to indicators.

At a temperature of 105° under atmospheric pressure, the chief

product is the mono-ester (35 per cent. of the phosphoric acid taken); the di-ester is also formed, the quantity reaching 6—7 per cent. when the heating is extended over 80 hours (compare Imbert and Belugou, Abstr., 1900, i, 130). Under atmospheric pressure at 125°, a small quantity of the tri-ester is formed; the amount increases as the pressure is diminished, until at a temperature of 115° under 0·01 mm. pressure it is the only product, and corresponds with 98·8 per cent. of the phosphoric acid taken. M. A. W.

Solubility of Salts. XII. Ammonium Hydrogen Formate. Erich Groschuff (*Ber.*, 1903, 36, 4351—4357).—According to Reik (Abstr., 1903, i, 308), ammonium formate does not yield an acid salt. The author having found (*ibid.*, i, 600) that potassium and sodium form hydrogen formates, has examined the ammonium salt,

$$HCO_2NH_4,CO_2H_2,$$

which is prepared by dissolving the normal salt in glacial formic acid and cooling to 0°. The crystalline salt decomposes at 23° into formic acid and the normal salt. Water begins to decompose it at 9—10°. The solubility of the normal salt in water is increased by the addition of formic acid. C. H. D.

Acetates of the Alkaline Earths. Albert Colson (*Compt. rend.*, 1903, **137**, 1061—1063. Compare Abstr., 1903, i, 396, 456, 601; this vol., i, 3).—A mixture of glacial acetic acid and acetic anhydride dissolves magnesia, forming the acetate $MgAc_2,1·5C_2H_4O_2$, identical with the salt obtained by dissolving magnesium in acetic acid. One hundred parts of acetic acid dissolve 10 parts of the salt at 15°.

Calcium hydrogen acetate, $CaAc_2,C_2H_4O_2$, exists in two forms, (1) a voluminous, amorphous substance obtained by the slow action of a mixture of glacial acetic acid and acetic anhydride on chalk, or by the action of pure acetic acid on chalk crystallised by fusion in the electric furnace; (2) hard, transparent crystals obtained by dissolving chalk in boiling acetic acid, or by leaving the amorphous form in contact with acetic acid for several weeks. One hundred parts of acetic acid dissolve 6—7 parts of calcium acetate at 100°, and half the quantity at 20°.

Neither calcium nor magnesium acetate forms an acetochloride; magnesium acetate in acetic acid solution is partially converted into magnesium chloride by the prolonged action of chlorine, or more readily by the action of chlorine and water. M. A. W.

Some Double Salts of Lead. John White (*Amer. Chem. J.*, 1904, 31, 1—24).—The *salt*, $PbI(C_2H_3O_2),NaC_2H_3O_2,\frac{1}{2}C_2H_4O_2$, obtained by heating a mixture of sodium acetate and lead iodide with 80 per cent. alcohol containing a small proportion of acetic acid, crystallises in white, flat, orthorhombic plates; another *salt*, $PbI(C_2H_3O_2),3NaC_2H_3O_2,\frac{1}{2}C_2H_4O_2$, is also produced and forms thin, pearly-white scales. The *salt*, $PbI(C_2H_3O_2),KC_2H_3O_2$, crystallises in pearly-white leaflets, and is probably identical with the compound obtained by Tommasi (Abstr., 1872, 242), to which he assigned the

formula $2PbI(C_2H_3O_2),KC_2H_3O_2$. The *salt*, $PbI(C_2H_3O_2),NH_4\cdot C_2H_3O_2$, crystallises in orthorhombic prisms; on evaporating the mother liquor, the double lead ammonium iodide described by Wells and Johnston (Abstr., 1893, 523) is obtained. The *salt*,

$$PbI(C_2H_3O_2),Pb(C_2H_3O_2)_2,\tfrac{1}{2}C_2H_4O_2,$$

forms well-defined, monoclinic prisms.

All these salts are almost instantaneously decomposed by water with formation of lead iodide and the basic iodide, $PbI(OH)$. E. G.

Complex Zirconium Compounds. ALFRED MANDL (*Zeit. anorg. Chem.*, 1903, 37, 252—302).—*Basic zirconium nitrate* is an amorphous, white mass, easily soluble in water. *Zirconium acetate* is best prepared by adding ammonium acetate and dilute ammonia to a cold solution of zirconium nitrate, then dissolving the precipitate in acetic acid, and finally evaporating this solution. *Zirconium carbonate* is prepared by passing carbon dioxide through an aqueous solution of zirconium nitrate and ammonium carbonate.

Zirconium nitrate solution gives a precipitate with the potassium salts of many organic acids. In order to decide whether soluble double salts or complex salts were formed, a solution of zirconium nitrate was added to a definite volume of a solution of the potassium salt of the acid until no more precipitate formed. The precipitate with formic, acetic, and butyric acids respectively did not redissolve on the addition of excess of zirconium nitrate, whilst the precipitate with glycollic, lactic, and glyceric acids respectively did. In the last two cases, more zirconium solution was required than corresponded with one carboxyl group. A large number of other acids have been studied in this direction and the results are recorded.

Zirconium potassium oxalate, $Zr(KC_2O_4)_4,5H_2O$, forms monoclinic prisms, easily soluble in water. *Zirconium ammonium oxalate*, $Zr(NH_4C_2O_4)_4,6H_2O$, forms monoclinic crystals. *Zirconium potassium malonate*, $Zr(CO_2\cdot CH_2\cdot CO_2K)_4,11H_2O$, is deliquescent and easily soluble in water. *Zirconium potassium maleate*,

$$Zr(CO_2\cdot CH{:}CH\cdot CO_2K)_4,H_2O,$$

is crystalline. *Zirconium potassium glycollate*, $ZrK_4(C_2H_3O_3)_8,3H_2O$, separates from alcohol in microscopic prisms. *Zirconium potassium malate*, $Zr(C_4H_3O_5K)_2,C_4H_6O_5,C_4H_5KO_5,4H_2O$, is easily soluble in water. *Zirconium potassium tartrate*, crystals with $10H_2O$, and separates in monoclinic crystals. *Zirconium potassium sodium tartrate* forms microscopic prisms. *Zirconium potassium citrate* forms monoclinic needles and crystallises with $9\tfrac{1}{2}H_2O$.

The composition of zirconium hydroxide, dried over sulphuric acid at the ordinary temperature, is $Zr(OH)_4$, whilst the hydroxide dried at 100° has the composition $ZrO(OH)_2$.

Zirconium potassium β-resorcylate crystallises with $4H_2O$.

The condition for the formation of double salts and complex compounds is that the carboxylic acid in question must have two contiguous carboxyl groupings. Certain hydroxy-carboxylic acids with low dissociation constants are quoted; these either do not form double salts at all or yield double salts of highly complex structure.

A. McK.

α-Iodopropionic Acid. WLADIMIR ZERNOFF (*Ber.*, 1903, **36**, 4392—4394).—Propionic acid and phosphorus pentachloride are dissolved in chloroform and warmed to 65°, and iodine monochloride is added in small quantities until free iodine begins to separate. The mixture is poured into ice-water, and shaken first with sodium carbonate solution, then for several hours with water. The solution is dried, the chloroform removed, and the acid crystallised from light petroleum. It forms small prisms, melts at 44·5—45·5°, and is readily soluble in all organic solvents. The same acid may be obtained by hydrolysing the ester obtained by the action of potassium iodide on ethyl α-bromopropionate.

Most of the salts are readily soluble, the *lithium* salt contains H_2O; the *magnesium* salt, $4\frac{1}{2}H_2O$; whilst the *copper* salt is anhydrous.

J. J. S.

Derivatives of Lauric Acid. GABRIEL GUÉRIN (*Bull. Soc. chim.*, 1903, [iii], **29**, 1117—1124).—The lauric acid was prepared from a by-product obtained in refining cocoanut oil, and was separated from the associated fatty acids by fractional distillation of the mixed methyl esters under reduced pressure.

Methyl laurate melts at 5° and distils at 148° under 18 mm. pressure. *Lauroyl*-o-*toluidide*, $C_{11}H_{23}\cdot CO\cdot NH\cdot C_6H_4Me$, crystallises from ether and melts at 81—82°; the p-*toluidide* melts at 82—83°, and the *phenylhydrazide*, which forms brilliant spangles, melts at 105° and becomes yellow on exposure to air and light.

Lauroyl chloride condenses with tetrachloroquinol to form *dilauroyltetrachloroquinol*, which melts at 83—84°.

Octoic acid was obtained as a by-product in the preparation of lauric acid. Octoyl chloride condenses with tetrachloroquinol to form *dioctoyltetrachloroquinol*, which melts at 74°.

T. A. H.

Purification of Esters of High Molecular Weight by Vacuum Distillation. FRIEDRICH KRAFFT (*Ber.*, 1903, **36**, 4339—4344).—The esters of the higher fatty acids give sharply-defined boiling points in the vacuum of the cathode light. The ethyl esters are comparatively volatile:

	B. p. under 0 mm. (25 mm. column).	B. p. under 0 mm. (65 mm. column).
Ethyl stearate	139°	154°
Ethyl palmitate	122	138
Ethyl myristate	102	121
Ethyl laurate	79	101

The ethylene esters, prepared by heating ethylene chloride with the dry potassium salts at 180°, crystallise from alcohol in colourless, glistening leaflets:

	M. p.	B. p. under 0 mm. (20 mm. column).
Ethylene distearate	79°	241°
Ethylene dipalmitate	72	226
Ethylene dimyristate	64	208
Ethylene dilaurate	54	188

When the potassium salts are heated for 12—15 hours with an excess of ethylene chloride at 135°, or with ethylene bromide at 120—130°, the chloro- and bromo-ethyl esters are obtained:

	M. p.	B. p. under 0 mm.
β-Chloroethyl palmitate	44°	138°
β-Bromoethyl palmitate	62	144
β-Chloroethyl myristate	34	115
β-Bromoethyl myristate	48	134
β-Chloroethyl laurate	24	100
β-Bromoethyl laurate	36	124

These esters react with amines, forming *β*-amino-esters.

The monoglycerides, prepared by heating the potassium salts with *a*-monochlorohydrin in sealed tubes in an atmosphere of carbon dioxide, may be distilled in small vacuum vessels. These compounds have not been previously obtained in a state of purity:

	M. p.	B. p. under 0 mm.
Monobenzoin, long crystals	36°	124°
Monolaurin, transparent, crystalline mass...	59	142
Monomyristin	68	162
Monopalmitin, crystallised from benzene ...	72	—
Monostearin, crystallised from benzene......	78	—
Mono-olein, white crystals	35	—

Benzoyl chloride and sodium hydroxide convert the monoglycerides into triglycerides. *Dibenzoylmonopalmitin*, $C_3H_5(OBz)_2 \cdot CO_2 \cdot C_{16}H_{31}$, melts at 69°, *dibenzoylmonomyristin*, $C_3H_5(OBz)_2 \cdot CO_2 \cdot C_{13}H_{27}$, crystallises from alcohol in white leaflets and melts at 65°.

The method may also be employed to isolate pure triglycerides from crude fats. In this way, pure trilaurin was obtained from laurel oil, and trimyristin from Japanese wax. Tripalmitin and stearin undergo slight decomposition when distilled, even under such low pressures.

C. H. D.

Nitric Esters of Hydroxy-acids. HENRI DUVAL (*Compt. rend.*, 1903, **137**, 1262—1264).—*Glycolloglycollic acid nitrate*, $NO_2 \cdot O \cdot CH_2 \cdot CO \cdot O \cdot CH_2 \cdot CO_2H$, an amber-coloured oil, soluble in water, alcohol, or ether, slightly so in benzene, and insoluble in light petroleum, is formed as a secondary product in the nitration of glycollic acid (compare Abstr., 1903, i, 603, 676).

Lactic acid nitrate, $NO_2 \cdot O \cdot CHMe \cdot CO_2H$, is obtained by adding zinc lactate to a mixture of fuming nitric and concentrated sulphuric acids; after extracting with ether and drying for two weeks in a vacuum, the ester is obtained as a pale yellow oil, miscible with water, alcohol, ether, or benzene, and insoluble in ligroin.

a-Hydroxybutyric acid nitrate, $CH_2Me \cdot CH(O \cdot NO_2) \cdot CO_2H$, prepared similarly to the lactic acid nitrate, is a crystalline, colourless solid

melting at 45° and extremely soluble in water, alcohol, ether, or benzene, less so in light petroleum.

Methyl nitroglycollate, $NO_2 \cdot O \cdot CH_2 \cdot CO_2Me$, is a colourless liquid with an agreeable colour, neutral to litmus, boiling with decomposition at 165° under the ordinary pressure and at 82·5° under 28 mm. pressure; it is soluble in alcohol, ether, or benzene, insoluble in water and light petroleum. M. A. W.

α-Hydroxylauric Acid. GABRIEL GUÉRIN (*Bull. Soc. chim.*, 1903, [iii], 29, 1124—1128).—*α-Hydroxylauric acid*, prepared by brominating lauroyl chloride, treating the resulting product with water, and hydrolysing the α-bromolauric acid so formed with an aqueous solution of potassium hydroxide, is crystalline and melts at 73—74°. The *sodium*, *potassium*, *copper*, and *lead* salts were prepared; the *ethyl* ester melts at 43°.

α-Acetoxylauric acid melts at 47°, the *ethyl* ester is a liquid and boils at 172—173° under 13 mm. pressure.

α-Hydroxylauroylanilide melts at 83° and the p-*toluidide* at 100°.

T. A. H.

Stereoisomerism in the Esters of Substituted Camphocarboxylic Acids and Methylhomocamphoric Acid. Ethylcamphocarboxylic Acid. JULES MINGUIN (*Compt. rend.*, 1903, **137**, 1067—1069).—When methylcamphocarboxylate is methylated, there is formed in addition to the solid α-methyl methylcamphocarboxylate, m. p. 85°, $[\alpha]_D + 17·25°$ (Abstr., 1891, 1500), a liquid product from which the author has extracted a liquid stereoisomeride, *β-methyl methylcamphocarboxylate*, boiling between 135° and 140° under 13 mm. pressure, and having $[\alpha]_D + 75°$. It is saponified by alcoholic potash in sealed tubes at 180°, yielding methylcamphor identical with that given by the α-compound under the same conditions (Abstr., 1892, 1343).

When methyl camphocarboxylate is treated with ethyl iodide and sodium methoxide, a liquid is obtained boiling at 167° under 10 mm. pressure; this is a mixture of the α- and β-stereoisomerides of methyl ethyl camphocarboxylate, the α-isomeride melts at 60° and has $[\alpha]_D + 58°$; the β-compound is a liquid boiling at 162° under 10 mm. pressure and has $[\alpha]_D + 87·8°$ (compare Brühl, Abstr., 1903, i, 6, 64; Haller, Abstr., 1903, i, 503). Each isomeride is saponified by alcoholic potash at 220°, forming ethylcamphor and small quantities of ethylcamphocarboxylic acid.

α-Methylhomocamphoric acid, $CO_2H \cdot C_8H_{14} \cdot CHMe \cdot CO_2H$, m. p. 178—180°, $[\alpha]_D + 26·31°$, has been prepared by the action of alcoholic potash on methylcyanocamphor (compare Haller and Minguin, Abstr., 1894, i, 338). The stereoisomeric β-derivative is obtained together with methylcamphor when methyl methylcamphocarboxylate is saponified in sealed tubes at 200°; it melts at 143° and has $[\alpha]_D + 38·12°$ (compare Rochussen, *Inaug. diss.*, 1897, Bonn; Brühl, Abstr., 1903, i, 6).

An attempt to prepare β-ethylhomocamphoric acid by saponifying methyl ethylcamphocarboxylate at 220° was unsuccessful; *ethylcampho-*

carboxylic acid, $C_8H_{14}<\begin{array}{l}CEt\cdot CO_2H\\ |\\ CO\end{array}$, crystallising in needles, was the only product. M. A. W.

Camphocarboxylic Acid. VIII. Julius W. Brühl (*Ber.*, 1903, 36, 4272—4294. Compare Abstr., 1903, i, 548).—The *benzoyl* derivative of *methylcamphocarboxylate*, $C_8H_{14}<\begin{array}{l}C\cdot CO_2Me\\ \|\\ C\cdot OBz\end{array}$, crystallises from alcohol in rhombic plates, melts at 58·5—59·5°, and gives, in alcoholic solution, no ferric chloride coloration. It is a benzoate and not a *C*-benzoyl derivative, since its saponification products are camphocarboxylic acid and benzoic acid.

When methyl bromocamphocarboxylate, $C_8H_{14}<\begin{array}{l}CBr\cdot CO_2Me\\ |\\ CO\end{array}$, in ethereal solution is acted on by sodium, a yellowish-white residue is obtained, which on benzoylation yields the benzoate. Enolisation had accordingly occurred during the action of sodium on the bromo-ester. The action of magnesium is partly analogous, although the magnesium does, to a slight extent, directly displace the bromine, attaching itself directly to carbon.

When methyl bromo-(or iodo-)camphocarboxylate is acetylated by magnesium and acetyl chloride according to Grignard's method, the presence of the *C*-acetyl derivative of methyl camphocarboxylate can be detected in the reaction product, and acetylcamphor was isolated as the product of its hydrolysis. The free bromocamphocarboxylic acid did not form a *C*-acetyl derivative when acted on by magnesium and ethyl acetate.

An ethereal solution of iodoformylcamphor was gradually added to magnesium, which was covered by dry ether, in an atmosphere of dry carbon dioxide. Hydroxymethylenecamphor was formed by the action of water on the product, thus:

$$C_8H_{14}<\begin{array}{l}CI\cdot CH{:}O\\ |\\ CO\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C\cdot CH{:}O\\ \|\\ C\cdot OMgI\end{array} \rightarrow$$

$$C_8H_{14}<\begin{array}{l}C\cdot CH{:}O\\ \|\\ C\cdot OH\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}CH\cdot OH\\ |\\ CO\end{array}.$$

When the reaction is accelerated, the carbon dioxide does, however, play a part, the compound $C_8H_{14}<\begin{array}{l}C\cdot CH{:}O\\ \|\\ C\cdot O\cdot CO_2MgI\end{array}$ being probably formed.

When an ethereal solution of *oo*-dibromocamphor is acted on by magnesium in the presence of iodine and in an atmosphere of carbon dioxide, and the reaction product decomposed by water, camphocarboxylic acid is formed. *oo*-Di-iodocamphor behaves similarly.

Ethyl ethylacetoacetate can be extracted by ether from its aqueous solution in ice-cold 2 per cent. sodium hydroxide. Methyl camphocarboxylate behaves similarly. These two esters also resemble one

another in being more readily saponified by aqueous alkalis than is ethyl acetoacetate itself.

A *résumé* of the author's work on enolic derivatives of camphor is given. A. McK.

Splitting off of Hydrogen Ions from Methylene Groupings. JULIUS WAGNER and FELIX HILDEBRANDT (*Ber.*, 1903, **36**, 4129—4131. Compare Vorländer, Abstr., 1903, i, 230; Ehrenfeld, Abstr., 1903, i, 548).—$N/10$ solutions of potassium tetroxalate, succinic acid, and citric acid respectively required the same amount of baryta for neutralisation. Such was also the case when $N/50$ solutions of potassium tetroxalate, tartaric, salicylic, and benzoic acids respectively were employed. Malonic acid, however, on titration in the cold with baryta, gave the same value as potassium tetroxalate, but the amount of baryta necessary for neutralisation diminished when the solution of malonic acid was heated, instead of increasing, as would be expected from Ehrenfeld's results. The authors surmise that malonic acid in a boiling aqueous solution undergoes slow decomposition into acetic and carbonic acids. A. McK.

Oxalates of Tervalent Thallium. W. OTTO RABE and HERMANN STEINMETZ (*Zeit. anorg. Chem.*, 1903, **37**, 88—112. Compare Abstr., 1902, ii, 491; 1903, i, 146).—A precipitate is formed when oxalic acid is added to a solution of a thallic salt, and in this respect thallium resembles scandium, yttrium, and lanthanum. Tervalent thallium tends to form acid oxalates, but not normal salts, and in this respect resembles aluminium, iron, and chromium.

Thallic oxalate, $Tl_2(C_2O_4)_3$, prepared by adding an alcoholic solution of anhydrous oxalic acid to an alcoholic solution of thallic formate, was obtained as an amorphous precipitate. When oxalic acid is gradually added to thallic hydroxide, suspended in water, the *acid oxalate*, $Tl(C_2O_4)_2H,3H_2O$, is obtained as a stable, white powder, which does not readily suffer hydrolytic dissociation, and which gives metallic thallium on being heated above 200°. It is instantly decomposed by aqueous alkalis. The *thallous thallic* salt, $Tl_2(C_2O_4)_2,3H_2O$, prepared by warming an aqueous solution of oxalic acid with thallic oxide, is soluble in water with difficulty, and from the solution thallic oxide is precipitated by the addition of alkali. When thallic hydroxide is allowed to remain at the ordinary temperature for several weeks with potassium hydrogen oxalate, a finely crystalline *potassium thallic oxalate*, $KTl(C_2O_4)_2,3H_2O$, is formed. *Ammonium thallic oxalate*, $NH_4Tl(C_2O_4)_2,2H_2O$, prepared in an analogous manner, parts with its water of crystallisation with difficulty. The *pyridine thallic oxalate*, $(C_5NH_6)Tl(C_2O_4)_2$, was also prepared. When an excess of oxalic acid is added to a solution of thallic hydroxide in concentrated nitric acid, the *thallic hydrogen oxalate*, $H_4Tl_2(C_2O_4)_5,6H_2O$, is precipitated. The *pyridine thallic oxalate*, $(C_5NH_6)_3Tl(C_2O_4)_3$, is also described (compare Abstr., 1903, i, 146); by the action of ammonia on a concentrated ethereal solution of this compound, *ammonium thallic oxalate*, $(NH_4)_3Tl(C_2H_4)_3$, is formed. When thallic oxalate is dissolved in a concentrated solution of potassium nitrite, a yellow, crystalline *salt* $K_3Tl(C_2O_4)_2(NO_2)_2,H_2O$, separates; it readily suffers hydrolytic disso-

ciation. The *compound*, $NH_4Tl(C_2O_4)_2,2NH_3$, is prepared by passing ammonia into an alcoholic solution of thallic hydrogen oxalate at 0°. The *compounds* $Tl_2(C_2O_4)_2,2NH_3$; $KTl(C_2O_4)_2,2NH_3$;

$$(C_5NH_6)Tl(C_2O_4)_2,(C_5NH_5)_2$$

are also described. A. McK.

Electrolytic Synthesis of Glutaric Acid. L. Vanzetti and Angelo Coppadoro (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 209—215).—Using as cathode solution, molecular proportions of ethyl succinate and malonate dissolved in water, and as anode liquid a 30 per cent. aqueous potassium carbonate solution, the authors obtain as products of electrolysis with platinum electrodes, the ethyl esters of succinic, glutaric, and adipic acids, together with a small proportion of an unsaturated ester (? ethyl acrylate). T. H. P.

Complete Synthesis of Camphoric Acid and Dehydrocamphoric Acid. Gustav Komppa (*Ber.*, 1903, 36, 4332—4335).—On methylating methyl diketo*apo*camphorate, $\begin{matrix} CO\cdot CH(CO_2Me) \\ | \\ CO\cdot CH(CO_2Me) \end{matrix}\!\!>CMe_2$ (Abstr., 1901, i, 668), with sodium (1 atom) and methyl iodide, an oil is obtained from which aqueous sodium carbonate extracts principally *methyl diketocamphorate*, $\begin{matrix} CO{-}CH(CO_2Me) \\ | \\ CO\cdot CMe(CO_2Me) \end{matrix}\!\!>CMe_2$, the *copper* salt of which, $C_{24}H_{30}O_{12}Cu$, is soluble in ether and thus renders purification easy. The ester, $C_{12}H_{16}O_6$, liberated from the copper salt, crystallises from methyl alcohol in beautiful, thick, apparently monoclinic plates, melts at 85—88°, and on reduction with sodium amalgam gives *dihydroxycamphoric acid*, $\begin{matrix} OH\cdot CH\cdot CH(CO_2H) \\ | \\ OH\cdot CH\cdot CH(CO_2H) \end{matrix}\!\!>CMe_2$, in the form of a syrup; the *barium* and *silver* salts were analysed. On reducing this acid with hydriodic acid of sp. gr. 1·7, a crystalline, racemic *dehydrocamphoric acid*, $\begin{matrix} CH{=\!=}C(CO_2H) \\ | \\ CH_2\cdot CMe(CO_2H) \end{matrix}\!\!>CMe_2$ or $\begin{matrix} CH{-}CH(CO_2H) \\ \| \\ CH\cdot CMe(CO_2H) \end{matrix}\!\!>CMe_2$, is obtained, which crystallises from very dilute alcohol in stellate aggregates of microscopic prisms, melts at 221—223°, and combines with hydrogen bromide in glacial acetic acid solution at 120—125° to form a *β-bromocamphoric acid*, $\begin{matrix} CHBr\cdot CH(CO_2H) \\ | \\ CH_2{-}CMe(CO_2H) \end{matrix}\!\!>CMe_2$(?). This, on reduction with zinc dust and acetic acid, gives racemic camphoric acid identical in every respect with Chautard's substance.

The *compound* $\begin{matrix} OMe\cdot C{=\!=}C(CO_2Me) \\ | \\ CO\cdot CMe(CO_2Me) \end{matrix}\!\!>CMe_2$ is formed simultaneously with methyl diketocamphorate in the original methylation; it is a colourless liquid which boils at 167—168° under 12 mm. pressure, and on reduction with sodium amalgam gives the dihydroxycamphoric acid already described. W. A. D.

Chemico-Physical Properties of the Malates of the Alkaline Earths. Ludovico Cantoni and Veratietti (*Gazzetta*, 1903, **33**, ii, 139—145).—The authors have made a number of experiments on the separation of barium, calcium, and strontium malates from solutions in presence of ammonia. Three principal factors are found to come into play, namely, the concentration, temperature, and nature of the solution. The method of preparation employed is expressed by the equation: $MCl_2 + C_4H_6O_5 + 2NH_3 = 2NH_4Cl + C_4H_4O_5M$; M being the alkaline earth metal. The results obtained are tabulated.

T. H. P.

Derivatives of Comenic Acid. A. Tamburello (*Gazzetta*, 1903, **33**, 264—266).—When concentrated ammonia is added to ethyl comenate, it dissolves, and, on adding silver nitrate, a comparatively stable *silver* salt is precipitated, which can be washed without decomposing; on agitating this salt with cold alcoholic ethyl iodide, *ethyl comenamide*, $OEt{\cdot}C_5H_2O_2{\cdot}CO{\cdot}NH_2$, is obtained, which separates from alcohol in white, lustrous crystals and melts at 159—160°.

The following compounds were obtained from the ordinary silver salt of ethyl comenate (Oliveri, Abstr., 1900, i, 587) by the action of alkyl iodides.

Ethyl comenate amyl ether, $C_5H_{11}O{\cdot}C_5H_2O_2{\cdot}CO_2Et$, crystallises from alcohol in large, hard, white prisms and melts at 79—80°. *Ethyl comenate* iso*propyl ether* crystallises in minute, white needles and melts at 123°.

W. A. D.

Undecaldehyde. Edmond E. Blaise and Gabriel Guérin (*Bull. Soc. chim.*, 1903, [iii], **29**, 1202—1208).—*Undecaldehyde*, $C_{10}H_{21}{\cdot}CHO$, was prepared from hydroxylauric acid by a slight modification of Baeyer's method (Abstr., 1897, i, 588). It is crystalline, has a characteristic, persistent odour, melts at $-4°$, and polymerises spontaneously, but more rapidly on addition of a few drops of sulphuric acid. The *polymeride*, $(C_{11}H_{22}O)_3$, is odourless, crystallises in needles or lamellæ, melts at 47—48°, has n_D 1·4322 at 23° and a sp. gr. 0·8251 at 23°/4°. The aldehyde gives all the usual colour reactions of the aliphatic aldehydes, does not combine with sodium hydrogen sulphite, being polymerised by this reagent, and condenses with β-naphthylamine and pyruvic acid (compare Doebner, Abstr., 1894, 261) to form *2-decyl-β-naphthacinchoninic acid*, which can be crystallised from methyl alcohol. With semicarbazide hydrochloride, undecaldehyde furnishes a *semicarbazone*, which is crystalline and melts at 103°; the *oxime* crystallises from methyl alcohol in white needles and melts at 72°.

Diundecylideneazine, $N_2(:CH{\cdot}C_{10}H_{21})_2$, obtained by condensing the aldehyde with hydrazine, melts at 57° and is very soluble in light petroleum. Undecaldehyde, when reduced by Krafft's method (Abstr., 1883, 1075), gives *undecyl alcohol*, which has a pleasant odour, boils at 146° under 30 mm. pressure, melts at 11°, has a sp. gr. 0·8334 at 23°/4° and n_D 1·4392 at 23°, and a crystalline condensation product of the alcohol, having the composition $C_{22}H_{46}O$. T. A. H.

Methyl Undecyl Ketone. Gabriel Guérin (*Bull. Soc. chim.*, 1903, [iii], 29, 1128—1131).—When ethyl sodioacetoacetate is treated with lauryl chloride and the resulting mixture of *O*- and *C*-esters is hydrolysed by an aqueous solution of potassium hydroxide, methyl undecyl ketone is formed from the *C*-ester (compare Bouveault and Bongert, Abstr., 1901, i, 311).

The *oxime* crystallises from ether on addition of light petroleum, is very soluble in alcohol and chloroform, less so in ether, and almost insoluble in benzene, and melts at 56—57°. The *semicarbazone* crystallises from boiling methyl alcohol and melts at 123°. T. A. H.

Ethyl Undecyl Ketone. Edmond E. Blaise and Gabriel Guérin (*Bull. Soc. chim.*, 1903, [iii], 29, 1208—1211).—*Lauronitrile*,

$$C_{11}H_{23}\cdot CN,$$

obtained by dehydrating lauramide with phosphoric oxide, has a characteristic, persistent odour, melts at 4°, and distils at 198° under 100 mm. pressure. When treated with metallic magnesium and ethyl iodide by the general method already described (Abstr., 1902, i, 164), it furnishes *ethyl undecyl ketone*, $C_{11}H_{23}\cdot COEt$. This is crystalline, melts at 34°, and distils at 152° under 16 mm. pressure; its *oxime* melts at 40°, and the *semicarbazone* at 92°. Both these derivatives crystallise well from methyl alcohol. T. A. H.

Action of Phosphorus Pentachloride on Methyl Undecyl Ketoxime. Edmond E. Blaise and Gabriel Guérin (*Bull. Soc. chim.*, 1903, [iii], 29, 1211—1216. Compare preceding abstracts).—When methyl undecyl ketoxime, $C_{11}H_{23}\cdot CMe\colon NOH$, dissolved in ether, is treated with phosphorus pentachloride, but little action occurs unless the latter is present in large excess and the mixture is boiled. In these circumstances, *acetylundecylamide*, $C_{11}H_{23}\cdot NHAc$ (which forms minute needles, melting at 47—48°), is the only amide produced, and on hydrolysis furnishes undecylamine and acetic acid. This result indicates that undecyl methyl ketoxime is homogeneous and not a mixture of stereoisomerides.

The authors suggest that the different behaviour of aliphatic ketoximes towards phosphorus pentachloride may be explained by assuming that in this reaction there is a tendency to form the amide of the more energetic acid, that is, the one having the alkyl group of less mass. Where the two alkyl groups of the ketoxime are not very dissimilar in mass, two amides are formed, but in different proportions. This suggestion is in accordance (*a*) with the formation of undecylacetamide from methyl undecyl ketoxime, (*b*) with Hantzsch's observation that all ketoximes having methyl as one alkyl group furnish a substituted acetamide, and (*c*) with the observation that from methyl ethyl ketoxime 66 per cent. of ethylacetamide and 33 per cent. of methylpropionamide are obtained (Hantzsch, Abstr., 1892, 426).

A similar rule probably also governs the hydrolytic decompositions of the acylacetoacetic esters studied by Bouveault and Bongert (Abstr., 1901, i, 311; 1903, i, 63, 141, and 142).

In the case of transformation of the oximes, however, some influence

appears to be exerted also by the reagent employed (compare Houben, Abstr., 1903, i, 47). T. A. H.

Action of Semicarbazide on Unsaturated Ketones. HANS RUPE and PAUL SCHLOCHOFF (*Ber.*, 1903, **36**, 4377—4384. Compare Rupe and Lotz, Abstr., 1903, i, 841).—The compound obtained by the condensation of citronellideneacetone with two molecules of semicarbazide (*loc. cit.*) is represented as having the constitution

$$CH_2{:}CMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH_2{\cdot}\underset{NH\cdot CO\cdot NH\cdot NH_2}{CH}{\cdot}CH_2{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

and is termed *citronellideneacetonesemicarbazidesemicarbazone.*

Mesityl oxide yields a similar *compound*,

$$NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

which crystallises in small, colourless plates, melting at 220°, and dissolves in dilute hydrochloric acid, but is practically insoluble in the ordinary organic solvents. When boiled with water, an odour of mesityl oxide is noticed, and hydrazidocarbonamide (Thiele, Abstr., 1892, 1298, 1429) and Scholtz's (Abstr., 1896, i, 343) and Harries' (Abstr., 1899, i, 637) compound melting at 129° are obtained.

Acetic anhydride converts the compound into acetylsemicarbazide, and nitrous acid yields a *nitrosoamine* melting at 146°. Benzylideneacetone, cinnamoylacetone, and pulegone yield the ordinary semicarbazones, which do not react with a second molecule of semicarbazide. This is probably due to the presence of the phenyl radicle.

Phorone also reacts with semicarbazide (2 mols.), yielding the *compound*

$$CMe_2{:}CH{\cdot}C({:}N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}CMe_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2,$$

which may be crystallised from hot water; it melts at 221°, is hydrolised by hydrochloric acid, and shows no tendency to undergo ring formation (Harries, Abstr., 1897, i, 211). When treated with sodium nitrite and hydrochloric acid, it yields a *nitroso*-derivative melting at 140°, together with a second compound melting at 169°.

J. J. S.

Compounds of Sucrose with Metallic Salts. D. GAUTHIER (*Compt. rend.*, 1903, **137**, 1259—1260).—The author has prepared a number of crystalline compounds of sucrose and the halogen salts of the alkali metals and of the metals of the alkaline earths. The compound with potassium iodide, $C_{12}H_{22}O_{11},KI,2H_2O$, forms crystals several centimetres in length. The compounds with the three lithium haloids have the general formula $C_{12}H_{22}O_{11},LiX,2H_2O$. Calcium bromide and iodide form compounds of the type

$$C_{12}H_{22}O_{11},CaX_2,3H_2O.$$

The sucrose compounds with strontium chloride and bromide are crystalline, but take a long time to form, whilst the three barium haloids yield voluminous crystalline compounds which are anhydrous and have the general formula $2C_{12}H_{22}O_{11},BaX_2$. M. A. W.

Nitrocelluloses. CARL HAEUSSERMANN (*Ber.*, 1903, **36**, 3956).—When collodion cotton, gun-cotton, or nitrated sulphite-cellulose is distilled with aqueous sodium hydroxide or with baryta, strontia, or

lime water, a small quantity of a *substance* passes over which gives the ordinary reactions of an aldehyde. W. A. D.

Composition of Silver Compounds of Methylamine and Ethylamine existing in Solution. GUIDO BODLÄNDER and W. EBERLEIN (*Ber.*, 1903, 36, 3945—3951. Compare Bodländer and Fittig, Abstr., 1902, ii, 248).—Wuth's measurements (Abstr., 1902, i, 594) of the solubility of silver chloride and bromide in methylamine and ethylamine are incorrect throughout; the values obtained by the authors show that the product of the amount of dissolved silver haloid by its dissociation is proportional to the concentration of the free base and not to the fourth root of this. If the formula of the complex salt be $Ag_mB_nCl_m$, that of the complex iron is Ag_mB_n, and the formula of decomposition into free base and silver ions becomes $Ag^m.B^n = k_1D$, D denoting the amount of dissolved silver chloride. The concentration of the silver ions is determined by that of the chlorine ions according to the equation $Ag^mD^m = k_2{}^m$, where $k_2 = [Ag][Cl]$; whence $B^n = (k_1/k_2{}^m).D^{m+1}$. But experimentally B/D was found constant, and this is reconcilable with formula (i), when $m = 1$, $n = 2$, or $m = 2$, $n = 3$, and so on. The formula of the complex salt must therefore be AgB_2Cl, $Ag_2B_3Cl_3$, $Ag_3B_4Cl_3$, &c., and Wuth's formula, Ag_3BCl_3, is excluded.

By measuring the *E.M.F.* of concentration cells containing the same quantity of base with different amounts of silver nitrate and chloride, using the formula $E = 0{\cdot}058/m.\log D_1/D_2$, the value of m was found to be approximately unity; similarly, from the *E.M.F.* of cells containing different quantities of the base, using the formula $E = n/m\ 0{\cdot}058.\log B_2/B_1$, n was ascertained to be nearly 2. The formulæ of the complexes are therefore $Ag(NH_2Me)_2X$, and $Ag(NH_2Et)_2X$. W. A. D.

Synthesis of Betaines from Dialkylated Aminonitriles. AUGUST KLAGES and S. MARGOLINSKY (*Ber.*, 1903, 36, 4188—4194).—The methiodide of diethylaminoacetonitrile melts at 190—195° instead of at 205° (Abstr., 1902, i, 354); by moist silver oxide, it is hydrolysed to methyldiethylbetainenitrile, the *picrate* of which melts at 166—168°. The ethiodide, after repeated recrystallisation, melts at 184°. Triethylbetainenitrile forms a *picrate* crystallising from water in glistening needles melting at 193°, an *aurichloride* melting at 118—119°, and a *mercurichloride* melting at 130—131°.

The *methiodide* of α-diethylaminopropiononitrile melts at 195—196° and, when hydrolysed, forms *methyldiethylpropionobetaine*, which melts at 117—119° and gives an *aurichloride* melting at 200—202°. The *ethiodide* of this nitrile melts and decomposes at 178—179°; *triethylpropionobetaine* melts at 90—92°, and its *aurichloride* at 253°.

Diethylaminophenylacetonitrile, $NEt_2{\cdot}CHPh{\cdot}CN$, is a faintly yellow oil boiling at 142° under 16 mm. pressure, and having a sp. gr. 0·9736 at 19°/4°. It was not found possible to hydrolyse this to the corresponding acid, either the *amide*, which crystallises in colourless crystals melting at 142—143°, or mandelic acid and diethylamine being formed. The *methiodide* forms colourless needles melting at 128—129°;

a-phenylmethyldiethylbetaine, $NMeEt_2\!<\!\genfrac{}{}{0pt}{}{CHPh}{O}\!>\!CO$, separates as a white, hygroscopic powder.

Piperidoacetonitrile is a colourless oil boiling at 99—100° under 15 mm. pressure, which crystallises in glistening crystals melting at 19°, and has a sp. gr. 0·9678 at 14°/4°; the *methiodide* separates in colourless plates melting at 192—193°, and the corresponding *methylpiperidobetaine* is a colourless, hygroscopic powder, which melts at 116—118° and yields an *aurichloride* melting at 178—179°.

E. F. A.

Action of Amyl Nitrite on Ethyl β-Aminocrotonate. Hans Euler and Astrid Euler (*Ber.*, 1903, 36, 4246—4253).—The *ammonium* derivative of *ethyl γ-isonitroso-β-nitrosoaminocrotonate*, $NH_4\cdot O\cdot N\!:\!CH\cdot C(NH\cdot NO)\!:\!CH\cdot CO_2Et$, prepared by the action of amyl nitrite on ethyl β-aminocrotonate dissolved in ether, crystallises in colourless, glistening scales and melts and decomposes at 170°; the *monopotassium* derivative, $C_6H_8O_4N_3K,H_2O$, prepared by oxidising the ammonium derivative with potassium permanganate, forms minute, glistening, colourless needles and explodes at 233°; the *dipotassium* derivative, $C_6H_7O_4N_3K_2$, forms colourless needles and melts at 232°; the *dibarium* derivative, $C_6H_7O_4N_3Ba$, forms a heavy, insoluble, brown powder; the *monozinc* derivative, $(C_6H_8N_3O_4)_2Zn$, is sparingly soluble in hot water, insoluble in alcohol.

Ethyl γ-isonitrosoacetoacetate, $OH\cdot N\!:\!CH\cdot CO\cdot CH_2\cdot CO_2Et$, prepared by the action of nitrous acid on the ammonium derivative just described, forms transparent, volatile tablets and melts at about 50°.

A *compound*, $C_6H_8O_4N_2$, probably $N\!<\!\genfrac{}{}{0pt}{}{CH\cdot C\!:\!CH\cdot CO_2Et}{O\text{---}N\cdot OH}$, prepared by the action of hydrobromic acid on the ammonium derivative, forms colourless needles and melts without decomposition at 90°.

T. M. L.

Action of Amyl Nitrite on Ethyl β-Aminocrotonate. Hans Euler and Astrid Euler (*Ber.*, 1903, 36, 4366).—The compounds $C_6H_{12}O_4N_4$, melting at 170°, and $C_6H_{10}O_4N_2$, melting at 89—90°, prepared by the interaction of amyl nitrite and ethyl β-aminocrotonate, have already been obtained by W. Strecker (Dissertation Heidelberg, 1900).

E. F. A.

Copper Thiocyanocyanides. Hermann Grossmann (*Zeit. anorg. Chem.*, 1903, 37, 407—410).—The clear solution, obtained by dissolving mercuric chloride (1 mol.) and potassium thiocyanate (4 mols.) in water, contains potassium mercuric tetrathiocyanate, $K_2Hg(CNS)_4$, and potassium chloride; the addition of potassium cyanide (2 mols.) causes the precipitation of the salt $CuCN,2KCN.KCNS,\frac{1}{2}H_2O$ in brilliant, glistening needles. The *salt* $2CuCN,3KCNS$, prepared from cuprous cyanide and potassium thiocyanate, forms rhombic plates. The salt $2CuCN,3NH_4CNS$ also crystallises in rhombic plates.

Cuprous cyanide is soluble with difficulty in concentrated solutions of alkali haloids.

A. McK.

Halogen Thiocyanates. Relationships between the Rhodanic, Halogen, and Cyanogen Ions. HERMANN GROSSMANN (*Zeit. anorg. Chem.*, 1903, 37, 411—447).—Whilst mercuric thiocyanate is precipitated from a solution of mercuric nitrate and potassium thiocyanate, there is no precipitation when mercuric chloride is used, since the tendency of the nitrate to form complexes with the potassium salts present is less than that of the chloride. *Cadmium mercuric thiocyanate*, $CdHg(CNS)_4$, separates from water in tetragonal plates. Mercuric thiocyanate is readily soluble in hot concentrated solutions of potassium and ammonium chlorides respectively, and, on cooling, the *salts* $Hg(CNS)_2,NH_4Cl$ and $Hg(CNS)_2,KCl$ respectively separate. Both are decomposed by water with the regeneration of mercuric thiocyanate. A mixture of complex salts is formed when mercuric thiocyanate is dissolved in a concentrated solution of potassium bromide. When, however, mercuric thiocyanate (1 mol.) is dissolved in an aqueous solution of potassium bromide (2 mols.), the *salt* $Hg(CNS)_2,2KBr$, crystallising in needles, is produced. The ammonium salt, $Hg(CNS)_2,NH_4Br$, was also prepared.

The *salt* $KCNS,HgBr_2$ separates from an alcoholic solution of its components. When mercuric bromide is dissolved in concentrated barium thiocyanate solution, the *salt* $Ba(CNS)_2,2HgBr_2,5H_2O$ separates in glistening needles. The salt $2KCNS,HgI_2$ does not contain water of crystallisation. The *salt* $2NH_4CNS,HgI_2$ is also anhydrous. The following *compounds* were also prepared: $Cd(CNS)_2,2KCl$; $Cd(CNS)_2,2NH_4Cl$; $Cd(CNS)_2,NH_4Br,H_2O$; $Cd(CNS)_2,KBr,H_2O$; $Cd(CNS)_2,2KBr$; $Cd(CNS)_2,2NH_4Br$; $2NH_4CNS,CdI_2$, and $2KCNS,CdI_2$.

The substances described can be formulated according to Werner's system.

The tendency of the rhodanic ion to form complex ions is discussed.

The relationship of complex haloid salts to complex thiocyanates is close. A systematic classification of all the known complex thiocyanates is appended. A. McK.

Relative Stability of Carbonylferrocyanides towards Oxidising Agents. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1903, [iii], 29, 1158—1161. Compare Abstr., 1903, i, 238).—The author finds that potassium carbonylferrocyanide is much more stable towards oxidising agents than is potassium ferrocyanide; it is, for example, not attacked by potassium persulphate, and only slightly so by potassium permanganate or ozone in the absence of sulphuric acid. Similarly, nitric acid, at atmospheric temperature, produces little effect. In the presence of sulphuric acid, ozone liberates a small quantity of hydrogen cyanide, and potassium permanganate is rapidly decolorised, hydrogen cyanide being evolved even in the cold, and more rapidly as the temperature is raised to 40—50°. T. A. H.

Carbonylferricyanides. JOSEPH A. MULLER (*Bull. Soc. chim.* 1903, [iii], 29, 1161—1166. Compare Abstr., 1903, i, 238, and preceding abstract).—When a solution of potassium carbonylferrocyanide is vigorously agitated during 40 seconds in an atmosphere of chlorine, approximately one atom of chlorine is absorbed (apart from that

mechanically dissolved by the solution) by each molecule of the carbonylferrocyanide present. The resulting liquid is precipitated by solutions of copper salts, furnishing a *product* having the composition represented by the formula $Cu_6KFe_5(CO)_5(CN)_{25}$. This is a dark green, hygroscopic powder, in which the relation of "ferric" to "ferrous" iron is as 2 : 3, and which, when treated with an aqueous solution of sodium hydroxide, gives an intensely yellow liquid, which in presence of dilute sulphuric acid gives a blue coloration with a solution of potassium iodide in starch mucilage, a violet-blue precipitate with ferric chloride, a blue precipitate with ferrous chloride, a brownish-apple-green precipitate with copper acetate, and a brownish-lilac precipitate with cobalt nitrate. The alkaline liquid is unstable, decomposing slowly at atmospheric temperatures and more rapidly on warming, with the deposition of a precipitate containing ferric oxide, and the formation in solution of sodium ferrocyanide (1 part) and carbonylferrocyanide (3 parts).

It is probable that the first result of the action of chlorine on the potassium carbonylferrocyanide is the formation of potassium chlorocarbonylferrocyanide, $K_3FeClCO(CN)_5$, which, on addition of a soluble copper salt, is converted into the green salt already described, part of the chlorine forming potassium chloride and the rest being evolved in the free state.

When the action of chlorine on potassium carbonylferrocyanide is prolonged, carbon dioxide is evolved, and a considerable quantity of potassium ferricyanide is formed. This decomposition is accelerated by the presence of potassium carbonate. Hydrogen peroxide appears to react with potassium carbonylferrocyanide at 60° in a manner similar to chlorine. T. A. H.

Derivatives of α-Aminopropionitrile. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1903, [iii], 29, 1190—1196).—α-Aminopropionitrile is monobasic to methyl-orange, does not react with phenolphthalein, and behaves in an indefinite manner with litmus: the hydrochloride, *sulphate*, platinichloride, *picrate*, and *tartrate* were prepared, and are described. When α-aminopropionitrile sulphate, dissolved in water, is boiled with a slight excess of barium hydroxide for 5 or 6 hours, it is converted into alanine, without the formation of the coloured by-products obtained when the hydrolysis is effected with hydrochloric acid. Iminopropionitrile is similarly converted by barium hydroxide into the corresponding acid.

α-*Acetylaminopropionitrile*, CN·CHMe·NHAc, obtained by warming the nitrile, dissolved in benzene, with acetic anhydride, crystallises from alcohol in rectangular lamellæ, melts at 102°, and is soluble in water and ether. The corresponding *benzoyl* derivative crystallises in plates, melts at 108°, and is very soluble in alcohol, soluble in water, and less so in ether. *l*-Benzoylaminopropionitrile crystallises in brilliant needles, melts at 123·5°, has $[\alpha]_D$ −55·84° at 15° in alcohol, and on hydrolysis with barium hydroxide furnishes *r*-benzoylaminopropionic acid: the *dextro*-isomeride melts at 115—120° and has $[\alpha]_D$ + 41·3° under the same conditions.

When α-aminopropionitrile, dissolved in ether, is treated with

phenylcarbimide, there is formed *phenyl-α-cyanoethylcarbamide*,

NHPh·CO·NH·CHMe·CN,

which is crystalline, melts at 135°, and is converted by warming with alcohol and hydrochloric acid into α-phenyl-δ-methylhydantoin (Mouneyrat, Abstr., 1900, i, 644).

With methylthiocarbimide, α-aminopropionitrile gives a viscous *product*, which on hydrolysis furnishes αδ-dimethylthiohydantoin (Abstr., 1896, i, 149). Similarly, it condenses with phenylthiocarbimide to form *phenyl-α-cyanoethylthiocarbamide* (minute crystals), which is hydrolysed by hydrochloric acid to α-phenyl-δ-methylthiohydantoin (*loc. cit.*).

When r-*α-aminopropionitrile* d-*tartrate*, which crystallises in colourless needles containing $2H_2O$ and has $[\alpha]_D + 17{\cdot}3°$, is dissolved in three times its weight of water and there is added to the solution an equal volume of alcohol, a precipitate having $[\alpha]_D + 12{\cdot}6°$ is obtained; by the addition of ether to the mother liquor, a precipitate having $[\alpha]_D + 18°$ is separated, and finally, by evaporation of the filtrate, a residue having $[\alpha]_D + 23°$ is procured. The extreme fractions are the *d*-tartrates of *l*- and *d*-α-aminopropionitrile respectively. Both salts contain H_2O; the solubility of that of the *d*-base in 80 per cent. alcohol is 1·91 grams per 100 c.c., and that of the *l*-base in the same solvent 0·66 grams per 100 c.c.; the sulphate of the *l*-base has $[\alpha]_D - 11{\cdot}4°$, and that of the *d*-base $[\alpha]_D + 10°$. T. A. H.

Basicity of α-Aminonitriles. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1903, [iii], **29**, 1196—1198. Compare preceding abstract).—The author finds that the heat of neutralisation of aminoacetonitrile (Klages, Abstr., 1903, i, 469) by sulphuric acid is 19·86 Cal. at 21° and that of α-aminopropionitrile 20·55 Cal. at 14°, those of the corresponding amines, methylamine and ethylamine, being respectively 30·1 and 30·4 Cal. In both cases, the ethyl compound has the higher heat of neutralisation. The introduction of a cyanogen group in the α-position appears to reduce the heat of neutralisation of the parent amine by about 10 Cal. The salts of the two α-aminonitriles appear to undergo comparatively little dissociation on solution in water, since the values of the heats of neutralisation are but little affected by the state of dilution of the salt produced. T. A. H.

Unsaturated Acids of the Sorbic Series and their Transformation into Cyclic Hydrocarbons. OSCAR DOEBNER and H. STAUDINGER (*Ber.*, 1903, **36**, 4318—4326. Compare Abstr., 1902, i, 598).—Both cinnamenylacrylic and *allo*cinnamenylacrylic acids give the same substances when distilled with anhydrous barium hydroxide; these consist of the saturated hydrocarbons phenyl*cyclo*butadiene,

$CHPh{<}{\begin{matrix}CH\\|\\CH\end{matrix}}{>}CH_2$ or $CHPh{<}{\begin{matrix}CH\\CH_2\end{matrix}}{\gtrdot}CH$, and diphenyl*cyclo*octadiene,

which have already been described (*loc. cit.*), a phenylbutylene which boils at 73° under 18 mm. pressure, probably identical with the "phenylbutene" of Harries and de Osa (Abstr., 1903, i, 815), and an iso*cyclobutadiene*, $(C_{10}H_{10})_x$, formed in very small quantity, which melts at 100—101° and boils at 155—165° under 16 mm. pressure.

On distillation with quinoline, the same acids give rise only to unsaturated hydrocarbons, namely, phenylbutadiene and diphenyldibutadiene (bisphenylbutadiene, Liebermann and Riiber, Abstr., 1902, i, 669).

W. A. D.

Reduction of Dinitrobenzenes. JAKOB MEISENHEIMER (*Ber.*, 1903, 36, 4174—4177).—When a solution of *o*-dinitrobenzene in methyl-alcoholic potash is reduced with hydroxylamine, also dissolved in methyl alcohol, the liquid turns a deep bluish-violet colour, oxygen is evolved, and on the addition of dilute hydrochloric acid *o*-nitronitrosobenzene is obtained (compare Bamberger and Hübner, this vol., i, 115).

When *p*-dinitrobenzene is reduced in a similar manner, a yellow *potassium* salt, $OK\cdot NO:C_6H_4:NO\cdot OK$, is obtained. It is soluble in water, but the solution decomposes when heated, and when acidified yields *p*-nitronitrosobenzene melting at 118—119°. It is probable that the reduction takes place as represented by the scheme:

$$NO_2\cdot C_6H_4\cdot NO_2 \longrightarrow OH\cdot NO:C_6H_4:NO\cdot OH \longrightarrow NO\cdot C_6H_4\cdot NO_2.$$

J. J. S.

A New Chlorotrinitrobenzene. RUDOLF NIETZKI and WALDEMAR ZÄNKER (*Ber.*, 1903, 36, 3953—3955).—When 1-chloro-3 : 4-dinitrobenzene dissolved in 40 per cent. pyrosulphuric acid is added to a mixture of sulphuric monohydrate and nitric acid of sp. gr. 1·52, 1-*chloro*-3 : 4 : 6-*trinitrobenzene* is obtained, which crystallises from alcohol in yellow leaflets and melts at 116°; when gently warmed with ammonia, 1-chloro-4 : 6-dinitro-3-aminobenzene is formed. The displacement of the chlorine atom needs a higher temperature.

W. A. D.

Substituted Benzhydrol Derivatives and Ethyl Bromocyanoacetate. N. E. GOLDTHWAITE (*Amer. Chem. J.*, 1903, 30, 447—470).—When diphenylmethane is treated with bromine at a low temperature and in presence of iodine, the product consists of about 70 per cent. of the di-*p*-bromo-derivative, 27 per cent. of the *op*-dibromo-compound, whilst the remainder is probably the di-*o*-bromo-derivative.

Di-p-*bromodiphenylmethane*, $CH_2(C_6H_4Br)_2$, the constitution of which was proved by its conversion into di-*p*-bromobenzophenone, is a white, crystalline compound which melts at 64°, is soluble in the usual organic solvents, and is best recrystallised from light petroleum. When this substance is heated with bromine at 150°, *di*-p-*bromodiphenylmethyl bromide*, $CHBr(C_6H_4Br)_2$, is produced, which crystallises in slender needles, melts at 106—107°, is very soluble in alcohol, benzene, or chloroform, but less so in ether or light petroleum, and gives a deep red coloration with concentrated sulphuric acid.

Tetra-p-*bromotetraphenylethylene*, $C(C_6H_4Br)_2:C(C_6H_4Br)_2$, obtained by heating di-*p*-bromodiphenylmethyl bromide at 165°, crystallises from alcohol in small, white needles, melts at 248°, and is not affected by treatment with bromine. An attempt to effect its reduction by means of zinc dust and acetic acid was unsuccessful.

When di-*p*-bromodiphenylmethyl bromide is treated with sodium acetate dissolved in glacial acetic acid, *di*-p-*bromobenzhydryl acetate*,

$CH(C_6H_4Br)_2 \cdot OAc$, is produced, which crystallises in short, slender needles, melts at 70—72°, and is soluble in most organic solvents. *Di*-p-*bromobenzhydrol*, $CH(C_6H_4Br)_2 \cdot OH$, prepared by the action of alcoholic potassium hydroxide on the acetate, crystallises in long, slender, white needles, melts at 115—116°, is very soluble in ether, alcohol, or acetic acid, gives a red coloration with concentrated sulphuric acid, and is converted into di-*p*-bromobenzophenone by oxidising agents. When di-*p*-bromobenzhydrol is heated gradually to 300°, tetra-*p*-bromophenylethane and di-*p*-bromobenzophenone are produced, but when heated quickly to 250° in a current of dry air, di-*p*-bromobenzhydryl ether is obtained. If the compound is heated for 40 minutes at 300°, di-*p*-bromobenzophenone, di-*p*-bromodiphenylmethane, and probably tetra-*p*-bromotetraphenylethylene are formed, whilst if it is heated at 300° for 8 hours in a stream of carbon dioxide, a mixture is obtained probably consisting of di-*p*-bromobenzophenone, di-*p*-bromobenzhydryl ether, tetra-*p*-bromotetraphenylethylene, and the corresponding ethane derivative.

Di-p-*bromobenzhydryl ether*, $O[CH(C_6H_4Br)_2]_2$, best prepared by heating di-*p*-bromodiphenylmethyl bromide with water at 120° in a sealed tube, forms masses of short, radiating crystals, melts at 155—156°, and is readily soluble in benzene or chloroform; when heated with acetic acid, it is converted into di-*p*-bromobenzhydryl acetate.

Di-p-*bromobenzhydryl ethyl ether*, $CH(C_6H_4Br)_2 \cdot OEt$, a viscid, colourless oil with a characteristic, not unpleasant odour, boils at 228° under 16 mm. pressure and gives a deep red coloration with concentrated sulphuric acid; when heated at 300°, it undergoes decomposition with formation of ethyl alcohol, di-*p*-bromobenzophenone, and di-*p*-bromodiphenylmethane.

Di-p-*bromotriphenylmethane*, $CHPh(C_6H_4Br)_2$, obtained by the action of concentrated sulphuric acid on a mixture of di-*p*-bromobenzhydrol and benzene, crystallises in slender needles, melts at 100°, distils at 260° under 15 mm. pressure, and is easily soluble in all organic solvents.

The paper concludes with a detailed account of the preparation and properties of ethyl bromocyanoacetate, and the action of sodium, ethyl sodiocyanoacetate, ethyl sodioacetoacetate, ethyl sodiomalonate, and aniline on it (compare Nef, Abstr., 1898, i, 107). E. G.

[Formation of] Retene from Abietic Acid. ALBERT VESTERBERG (*Ber.*, 1903, **36**, 4200—4202).—Crystallised abietic acid was heated with half its weight of sulphur at 200°, subsequently at 250°, and distilled under about 20 mm. pressure. A small quantity of a yellow, crystalline distillate was obtained, which proved to be retene.

E. F. A.

Substituted Mercurammonium Iodides from Primary and Secondary Amines. MAURICE FRANÇOIS (*Compt. rend.*, 1903, **137**, 1069—1070).—Mercuric iodide reacts with primary amines and their salts to give the following series of compounds: (1) mercuriodides of the general formula $(NH_2R,HI)_n(HgI_2)_n$, for example, aniline mercur-

iodide NH_2Ph,HI,HgI_2; (2) mercurichloroiodides having the formula $(NH_2R,HI)_n(NH_2R,HCl)_n(HgI_2)_n$, for example, aniline mercurichloroiodide, $(NH_2Ph,HI)_2,NH_2Ph,HCl,HgI_2$; (3) crystalline dissociable compounds having the general formula $(NH_2R)_n(HgI_2)_n$, soluble in alcohol, ether, or excess of the base. When compounds of the last series are treated with a solution of sodium hydroxide, the hydrogen of the NH_2 group is replaced by mercury, and insoluble products result. Thus diphenylmercuridiammonium iodide, $2NH_2Ph,HgI_2$, gives trimercuridiphenyldiammonium iodide, $2NHgPh,HgI_2$.

Tertiary amines react readily with mercuric iodide, forming compounds of the type $(NR_3)_n(HgI_2)_n$, which contain no replaceable hydrogen, and are therefore not changed by the action of a solution of sodium hydroxide. Mercuripyridyldiammonium iodide, $(C_5H_5N)_2,HgI_2$, can be obtained in large, colourless crystals which are not altered by prolonged contact with a 25 per cent. sodium hydroxide solution in the cold; if, however, the mixture is heated by a current of steam, the mercuripyridyldiammonium iodide dissociates into pyridine, which is volatile in the steam, and mercuric iodide, which is converted into the oxyiodide in the ordinary way. M. A. W.

Action of Secondary Bases on the Carbonates of Phenols. Bouchetal de la Roche (*Bull. Soc. chim.*, [iii], 31, 19—21).—The secondary bases of the fatty series react with the carbonates of phenols to give the corresponding carbamates, $NR_2 \cdot CO_2 \cdot C_6H_4 \cdot X$. Diphenylamine, however, does not react in this way. *Phenyl diethylcarbamate*, is a colourless liquid, which boils at 150° under 15 mm. pressure. o-*Tolyl diethylcarbamate* is a colourless, crystalline substance melting at 52° and boiling at 178—179° under 15 mm. pressure. o-*Tolyl dipropylcarbamate* boils at 180° under 19 mm. pressure. p-*Tolyl dipropylcarbamate* is a colourless liquid which boils at 185° under 18 mm. pressure. *Guaiacol dipropylcarbamate* is also a liquid; it boils at 196° under 18 mm. pressure. *Phenyl dibenzylcarbamate* is a colourless oil, which distils at 282—284° under 23 mm. pressure. *Tolyl* and *guaiacol dibenzylcarbamates* were also prepared; they are viscous oils, which boil and decompose at above 300° under reduced pressure.

S. S.

Action of Phenylcarbimide on Certain Monohydric Alcohols. Armand Bloch (*Bull. Soc. chim.*, [iii], 31, 49—53).—By the action of phenylcarbimide on monohydric alcohols of high molecular weight, the corresponding phenylurethane was obtained in every case. *n*-Octyl phenylurethane, $NHPh \cdot CO_2 \cdot C_8H_7$, forms colourless prisms, which melt at 69° and are soluble in hot alcohol; sec.-*octyl phenylurethane* is a liquid; *undecyl phenylurethane*, $NHPh \cdot CO_2 \cdot C_{11}H_{23}$, melts at 55—55·5° and crystallises in colourless needles, soluble in light petroleum or methyl alcohol, easily so in alcohol, ether, benzene, or chloroform. *Cetyl phenylurethane*, $NHPh \cdot CO_2 \cdot C_{16}H_{33}$, is deposited from alcohol is the form of crystalline scales, melts at 73°, distils at 244—250° under 17·5 mm. pressure, and is almost insoluble in cold alcohol or light petroleum. *Myricyl phenylurethane*, $NHPh \cdot CO_2 \cdot C_{30}H_{61}$,

melts at 91·5°, is very unstable, and decomposes readily into its constituents. S. S.

Derivatives of Anilinoacetonitrile. TH. PARADIES (*Ber.*, 1903, 36, 4302—4305).—*Anilinothioacetamide*, $NHPh\cdot CH_2\cdot C(:NH)\cdot SH$, prepared by the action of alcoholic ammonium sulphide on anilinoacetonitrile, melts at 165°. When heated with concentrated sulphuric acid, it did not yield indoxyl.

Anilinoacetiminoethyl ether, $NHPh\cdot CH_2\cdot C(:NH)\cdot OEt$, prepared by the action of dry hydrogen chloride on an ethyl-alcoholic solution of anilinoacetonitrile, was obtained in the crude form, which was converted into the *hydrochloride* melting at 195°. The free iminoether cannot readily be obtained from the hydrochloride; it may, however, be obtained from the nitrile and hydroxylamine hydrochloride in alcoholic solution by the addition of sodium carbonate. It boils at 115—117° under 60 mm. pressure; its *nitroso*-derivative melts at 98°; its *sulphate* is soluble in water with difficulty.

Anilinoethenylamido-oxime, $NHPh\cdot CH_2\cdot C(:N\cdot OH)\cdot NH_2$, prepared from hydroxylamine and anilinoacetonitrile, separates from alcohol in rhombic crystals and melts at 147—148°; its *hydrochloride* melts at 174—175°. A. McK.

Phenylene- and Tolylene-diglycines. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145062).—Glycollonitrile, $OH\cdot CH_2\cdot CN$, reacts with *p*-phenylenediamine to form p-*phenylenediaminodiacetonitrile*, $C_6H_4(NH\cdot CH_2\cdot CN)_2$, which crystallises from alcohol in leaflets insoluble in water and melts at 170—171°. Dilute mineral acids or alkalis hydrolyse it to p-*phenylenediglycine*, $C_6H_4(NH\cdot CH_2\cdot CO_2H)_2$, which is insoluble in cold water, but dissolves in dilute acids or alkalis, and separates from a large excess of hot water in crystals melting and decomposing at 233—235°. The dinitrile dissolves in concentrated sulphuric acid forming p-*phenylenediaminodiacetamide*, $C_6H_4(NH\cdot CH_2\cdot CO\cdot NH_2)_2$, which separates in crystals on pouring the solution on to ice, and melts and decomposes at 270—275°; it is hydrolysed to *p*-phenylenediglycine by prolonged boiling with dilute solutions of the alkali hydroxides.

Hydrogen cyanide and formaldehyde may be employed in place of glycollonitrile. The *p*-phenylenediamine may be conveniently combined with formaldehyde to form a bluish-white, pulverulent *compound*, insoluble in water or alcohol, but dissolving in solutions of alkali hydrogen sulphites and melting and decomposing at 235°. Potassium cyanide reacts with a solution of the alkali hydrogen sulphite compound, giving a quantitative yield of phenylenediglycine.

p-*Tolylenediglycine* melts at 150—160°, and p-*tolylenediaminodiacetonitrile* at 100—103°. C. H. D.

Preparation of Phenylglycine and its Homologues. BASLER CHEMISCHE FABRIK (D.R.-P. 145376. Compare preceding abstract).—An alkaline alcoholic solution of methylenedianiline, $CH_2(NHPh)_2$, prepared by the condensation of aniline with formaldehyde (Eberhardt and Walter, Abstr., 1894, i, 451), reacts with potassium cyanide to form phenylglycine, ammonia being evolved. The yield is almost

quantitative. The homologues of phenylglycine may be prepared in a similar manner. C. H. D.

4 : 5-Dinitro-α-naphthylamine. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P 145191).—5-*Nitro-α-acetonaphthalide*, prepared by heating 5-nitro-α-naphthylamine with acetic acid and acetic anhydride, or by adding acetic anhydride to an aqueous suspension of nitronaphthylamine at 50—70°, crystallises from acetic acid in thick, brown prisms giving a bright yellow powder and melting at 220°. The *formyl* derivative is formed with great ease on merely warming the amine with formic acid, and crystallises in small, yellow needles melting at 199°. Nitration with nitric and sulphuric acid yields the *dinitro*-compound, crystallising from boiling glacial acetic acid in felted, yellow needles melting at 244°. 4 : 5-*Dinitro-α naphthylamine*, prepared by the hydrolysis of the acetyl derivative with dilute sulphuric acid, crystallises from acetic acid in brownish-orange leaflets melting at about 236°. C. H. D.

Derivatives of Diphenylenediphenylmethane. FRITZ ULLMANN and R. VON WURSTEMBERGER (*Ber.*, 1904, **37**, 73—78).—*Phenyldiphenylenecarbinol*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!CPh\cdot OH$, prepared from fluorenone and magnesium phenyl bromide, separates from light petroleum in transparent crystals, melts at 107°. and is easily reduced by zinc and acetic acid to phenyldiphenylenemethane, identical with Hemilian's product (Abstr., 1878, 431). The carbinol readily condenses with bases when boiled with them. *Phenyl-4′-aminophenyldiphenylenemethane*,

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!CPh\cdot C_6H_4\cdot NH_2,$$

prepared from aniline, crystallises from dilute alcohol, melts at 179°, and gives a crystalline *hydrochloride* which decomposes at 220—230°; the *acetyl* derivative crystallises from benzene and melts at 213·5°. *Diphenyldiphenylenemethane-4′-azodimethylan line*, prepared from the diazonium salt of the base and dimethylamine, forms large, red leaflets and melts at 192°.

Phenyl-4′-dimethylaminophenyldiphenylenemethane,

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!CPh\cdot C_6H_4\cdot NMe_2,$$

prepared by condensing the carbinol with dimethylaniline, crystallises from a mixture of benzene and light petroleum in stellate aggregates of large, slightly-coloured prisms and melts at 141·5°.

Phenyl-4′-methylamino-3′-tolyldiphenylenemethane,

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!CPh\cdot C_6H_3Me\cdot NHMe,$$

prepared from methyl-*o*-toluidine, crystallises from the same mixture in large, lustrous prisms and melts at 190·5°; the *hydrochloride* melts at 140—146° and decomposes at 160°.

Phenyl-4′-hydroxyphenyldiphenylenemethane, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!CPh\cdot C_6H_4\cdot OH$, obtained by adding concentrated sulphuric acid gradually to a solution of diphenylenephenylcarbinol and phenol in glacial acetic acid,

crystallises in a colourless, asbestos-like mass of needles and melts at 191°. W. A. D.

Additive Compounds with Dimethylaniline. C. Loring Jackson and Latham Clarke (*Ber.*, 1904, 37, 176—178. Compare Hepp, Abstr., 1883, 315).—The following additive compounds have been obtained.

1 : 3 : 5-*Trichlorotrinitrobenzene dimethylaniline* forms brownish-red prisms decomposing at 78°. 1 : 3 : 5-*Tribromotrinitrobenzene dimethylaniline*, crystallises in dark brown prisms decomposing at 50°. 3-*Bromo*-2 : 4 : 6-*trinitrotoluene dimethylaniline*, forms dark red prisms melting at 120°. 1 : 3 : 4 : 5-*Tetrachlorodinitrobenzene dimethylaniline*, forms orange-yellow prisms melting at 113°. *Ethyl* 4-*bromo*-3 : 5-*dinitrobenzoate dimethylaniline*, crystallises in broad, orange-red prisms melting at 56°. 1 : 3 : 5-*Tri-iododinitrobenzene dimethylaniline* forms pale yellow prisms melting at about 160°. 1 : 3 : 5-*Trianilinodinitrobenzene dimethylaniline* forms dark brown prisms melting at 120°.

The compounds are obtained by dissolving the nitro-compound in the base and adding alcohol ; as a rule, they cannot be recrystallised without undergoing decomposition. They also decompose when exposed to the air.

Chloranil dimethylaniline yields an additive compound which crystallises in short, dark blue prisms melting at 105°. *Trichloroquinone dimethylaniline* forms a blue compound melting at 65°.

[Similar, but much more stable, additive products have been obtained by Sudborough (Trans., 1901, 79, 522) and Hibbert and Sudborough (*ibid.*, 1903, 83, 1334)]. J. J. S.

Interaction between Nitrobenzene and Aniline in the Presence of Alkali. Alfred Wohl (*Ber.*, 1903, 36, 4135—4138. Compare Abstr., 1901, i, 612).—*p*-Nitrosodiphenylamine is obtained in addition to the products previously described when nitrobenzene and aniline are heated with finely-powdered, dry sodium hydroxide, first at 110—120° and then at 120—125°. When boiled with an aqueous solution of hydroxylamine hydrochloride, the nitroso-derivative is transformed into quinonedioxime.

The corresponding *nitroso*-derivative, obtained from *a*-naphthylamine, nitrobenzene, and an alkali hydroxide, crystallises in small, blue needles and melts at 143°. J. J. S.

Transformation of Diphenylnitrosoamine into *p*-Nitrosodiphenylamine. H. Raken (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 267—269).—The rate of transformation of diphenylnitrosoamine into *p*-nitrosodiphenylamine was examined by a colorimetric method, advantage being taken of the fact that the nitrosoamine has a faintly yellow colour, which in dilute solutions may be neglected, whilst the nitroso-base, in combination with hydrochloric acid, forms a brown powder, the dilute alcoholic solution of which is deep yellow, and more concentrated solutions dark brown or red. The experiments were made in alcoholic solution with hydrochloric acid as catalyser.

The reaction is of the first order. The reaction constant is proportional to the concentration of the hydrochloric acid. Addition of

water causes a large fall in the value of the constant. The temperature coefficient is very great.

The transformation in question is intramolecular. A. McK.

Action of Light on Dinitrobenzylideneaniline. FRANZ SACHS and EMIL SICHEL (*Ber.*, 1903, 36, 4373—4377).—2 : 4-Dinitrobenzylideneaniline, when exposed to the action of sunlight in benzene solution, forms two products, one melting at about 289°, of which the nature has not yet been established, and an orange-red substance melting at 180·5° and having the composition $C_{19}H_{14}O_3N_4$. This is shown to be *benzene*-o-*azo*-p-*nitrobenzanilide*, produced by intramolecular rearrangement of the anilide and subsequent exchange of oxygen for the group :NPh, derived from a second molecule of the benzylideneaniline, which is itself converted into dinitrobenzaldehyde ; the latter substance was proved to be among the products of the reaction. E. F. A.

Direct Preparation of *cyclo*Hexanol and *cyclo*Hexanone from Phenol. PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1903, 137, 1025—1027. Compare Abstr., 1901, i, 195, 263).—When a mixture of phenol and excess of hydrogen is passed over reduced nickel at 215—230°, *cyclo*hexanol is formed, which is partially decomposed by the nickel into *cyclo*hexanone (compare Abstr., 1903, i, 454). The mixture boils at 155—165°, and cannot be separated by fractional distillation.

Pure *cyclo*hexanone is prepared by passing the vapour of the mixture over reduced copper at 330°, the ketone is not affected, and the alcohol is converted into the ketone with liberation of hydrogen ; it is a colourless liquid with the odour of propanone and suggesting that of camphor ; it boils at 155·5° (corr.) and is identical with the compound prepared by Baeyer (Abstr., 1894, i, 175) and Markownikoff (Abstr., 1899, i, 23).

Pure *cyclo*hexanol is obtained from the mixture by passing its vapour, mixed with excess of hydrogen, over reduced nickel at 140—150° ; it solidifies under cold water, boils at 161° (corr.), and is identical with the compound prepared by Baeyer and Markownikoff (*loc. cit.*). M. A. W.

Oxidation of Mixed Organo-magnesium Compounds. Synthesis of Phenols. F. BODROUX (*Bull. Soc. chim.*, 1904, [iii], 31, 33—36).—Organo-magnesium compounds, R·MgX, rapidly absorb oxygen, forming substances of the general formula RO·Mg·X, which are decomposed by acids with liberation of a phenol or an alcohol. The present paper deals only with the oxidation of aromatic magnesium compounds and the preparation of the corresponding phenols. Air is bubbled through the ethereal solution of an organo-magnesium haloid until it becomes greenish-black in colour ; the phenol may then be extracted with an aqueous alkali hydroxide. The following phenols were synthesised, the figures in brackets giving the yields : phenol (18 per cent.), *o*-cresol (20 per cent.). *p*-cresol (15 per cent.), α-naphthol (12 per cent.), *p*-methoxyphenol (12 per cent.), *p*-ethoxyphenol (10 per cent.), 4-bromo-α-naphthol (22 per cent.), and 4-chloro-α-naphthol (21 per cent.). S. S.

A New Tri-iodophenol. P. Brenans (*Compt. rend.*, 1903, **137**, 1065—1067. Compare Abstr., 1901, i, 643; 1902, i, 280).—2 : 3 : 5-*Tri-iodo*-1-*nitrobenzene*, obtained in the usual way from 4 : 6-di-iodo-2-nitroaniline, crystallises in large, yellow prisms melting at 124°, is soluble in hot alcohol or methyl alcohol, and more so in the other ordinary solvents; it is reduced by stannous chloride to 2 : 3 : 5-*tri-iodoaniline*, which crystallises in colourless, silky needles melting at 116°, slightly soluble in ether or light petroleum, more so in benzene, alcohol, or acetic acid; its *acetyl* derivative crystallises in thin, silky needles which partially volatilise at 200° and melt at 227°; it is only slightly soluble in organic solvents. 2:3:5-*Tri-iodophenol*, prepared by diazotising 2 : 3 : 5-tri-iodoaniline, melts at 114° and is very soluble in organic solvents, but can be crystallised from a mixture of benzene and light petroleum; the *ethyl* ether, $C_6H_2I_3 \cdot OEt$, crystallises in thin, colourless, silky needles melting at 120°; the *acetyl* derivative forms colourless needles melting at 123° and is soluble in hot alcohol or acetic acid. M. A. W.

Preparation of 2-Nitroresorcinol. Hugo Kaufmann and Erwin de Pay (D.R.-P. 145190).—2-Nitroresorcinol is readily prepared by nitrating resorcinol-4 : 6-disulphonic acid at a low temperature. Resorcinol is dissolved in fuming sulphuric acid by warming, and after cooling to 0° a mixture of fuming sulphuric acid and nitric acid is added. When the mass has dissolved, water is added, and the nitroresorcinol is distilled in a current of superheated steam. The product obtained from acetometanilic acid is 4-nitroresorcinol.

C. H. D.

Action of Chlorosulphonic Acid on Guaiacol. Auguste Lumière and Louis Lumière and F. Perrin (*Bull. Soc. chim.*, 1903, [iii], **29**, 1228—1229).—When a well-cooled solution of guaiacol in chloroform is treated with chlorosulphonic acid, there is first formed o-*methoxyphenyl hydrogen sulphate* (the crystalline barium salt of this was prepared), but if the mixture be allowed to remain even for a few minutes, a white, crystalline, deliquescent precipitate of *guaiacolmonosulphonic acid* is produced. T. A. H.

Oxidation of Guaiacol by Laccase. Gabriel Bertrand (*Compt. rend.*, 1903, **137**, 1269—1272).—The compounds most readily oxidised by laccase are those of the cyclic series containing at least two OH or NH_2 groups situated in the ortho- or para-positions with reference to one another. Quinol is oxidised by laccase to quinone. The colour change effected in guaiacol by the juice of different fungi observed by Bourquelot (Abstr., 1897, ii, 66) is due to an oxidation brought about by the laccase which is present in the juice. The oxidation product is a *tetraguaiacoquinone* having the constitution $\begin{array}{l} O \cdot C_6H_3(OMe) \cdot C_6H_3(OMe) \cdot O \\ | \qquad\qquad\qquad\qquad\qquad\qquad | \\ O \cdot C_6H_3(OMe) \cdot C_6H_3(OMe) \cdot O \end{array}$; it is a fine, crystalline powder having a purplish-red colour with a faint green metallic lustre, insoluble in water, slightly soluble in ether, a little less so in alcohol, still less so in benzene, readily so in chloroform and acetic acid; all the solutions have the same mahogany-red colour and water reprecipitates the solid

from acetic acid solutions in the form of dense violet-purple flakes which melt between 135° and 140°.

Tetraguaiacoquinone is soluble in alkalis, forming coloured solutions; it is reduced by zinc and acetic acid forming *tetraguaiacoquinol*, $O_2[C_{12}H_6(OMe)_2{\cdot}OH]_2$, which is white and melts between 115° and 120°, its *diacetyl* derivative melts at 155—160° and it yields a *dimethyl* derivative. M. A. W.

1:2-Anthraquinol and its Conversion into Alizarin. Kasimir Lagodzinski (*Ber.*, 1903, 36, 4020—4022. Compare Abstr., 1894, i, 420; 1895, i, 544).—Zinc dust and acetic acid or other acid reducing agents reduce 1:2-anthraquinone to 1:2-*anthraquinol*, $C_{14}H_{10}O_2$, which crystallises from the hot filtered solution in greenish-yellow leaflets melting and decomposing at 131°, and dissolving readily in organic solvents to slightly fluorescent solutions. Oxidising agents reconvert it into the quinone; its alkaline solutions rapidly blacken in the air.

The position of the two hydroxyl groups being the same as in alizarin, the compound may be converted into alizarin by oxidation of its *diacetyl* derivative, $C_{18}H_{14}O_4$, melting at 145°, which is converted into diacetylalizarin by chromic acid. C. H. D.

Preparation of Hydroaromatic Alcohols. Léon Brunel (*Compt. rend.*, 1903, 137, 1268—1269. Compare Abstr., 1903, i, 695).—The paper contains the results already obtained by the author on the direct hydrogenation of substituted phenols in the presence of reduced nickel (compare Sabatier and Senderens, this vol., i, 156).

Phenol is converted almost quantitatively into *cyclo*hexanol, $C_6H_{11}{\cdot}OH$, when the liquid phenol is allowed to enter the tube containing the nickel at the rate of 12 grams per hour, with a current of hydrogen of 250 c.c. per minute, the tube being heated at 170—175°.

Under similar conditions, thymol is converted into *hexahydrothymol*, $C_{10}H_{19}{\cdot}OH$, the temperature of the tube being 180—185°. Hexahydrothymol is a syrupy, colourless liquid with an odour of mint, insoluble in water, soluble in alcohol or acetic acid, much less dense than water, and boiling at 214° under normal pressure.

Carvacrol is readily hydrogenated in the presence of reduced nickel at 195—200°; the product is *hexahydrocarvacrol*, $C_{10}H_{19}{\cdot}OH$, which is a syrupy, colourless liquid with an odour suggesting that of thyme; it is insoluble in water, soluble in alcohol, less dense than water, and boils at 218—219° under the ordinary pressure. M. A. W.

Phenylacetylcarbinol. E. Carapelle (*Gazzetta*, 1903, 33, ii, 261—264).—*Phenylacetylcarbinyl acetate*, $CH_3{\cdot}CO{\cdot}CHPh{\cdot}OAc$, prepared by the interaction of phenylbromoacetone, $CH_3{\cdot}CO{\cdot}CHPhBr$, with potassium acetate in absolute alcohol, is a yellow liquid which boils at 165—170° under 40 mm. pressure, and is hydrolysed by barium carbonate suspended in water, giving *phenylacetylcarbinol*, $CH_3{\cdot}CO{\cdot}CHPh{\cdot}OH$; this boils at 135° under 40 mm. pressure, reduces Fehling's solution and ammoniacal silver nitrate, and interacts with phenylhydrazine giving an *osazone* melting at 152—153°. When the foregoing acetate is hydrolysed with aqueous barium hydroxide, an intractable oil is obtained; a condensation product

similar to that obtained from acetylcarbinyl acetate by Peratoner and Leonardi (Abstr., 1900, i, 551) could not be isolated. W. A. D.

Crystallographic Characteristics of Isomeric Halogen and Nitro-derivatives of Benzoic Acid. F. M. JAEGER (*Chem. Centr.*, 1903, ii, 1173—1175; from *Zeit. Krist. Min.*, 38, 279—301. Compare Abstr., 1903, i, 240).—The original paper contains the results of crystallographic measurements of isomeric halogen and nitro-derivatives of benzoic acid collected from various sources, together with a large number of measurements of compounds not hitherto examined. The abstract contains only the latter. The isomeric chloro-nitro-acids which have the least equivalent volumes have also the most symmetrical crystalline forms. When several isomeric derivatives are formed simultaneously in certain chemical reactions, the crystalline forms of these substances usually appear to have the same symmetry and similar parameters. In the series of derivatives of 4-chloro-3-nitrobenzoic acid, successive substitution in the carboxyl group causes elongation of the crystals in the direction of the *a* and *b* axes, but decrease along the *c* axis, finally attaining a limit in the methylamide; the substitution of two H atoms in the NH_2 group by CH_3 groups has, however, an opposite effect. The crystalline forms of the derivatives of the 2 : 4 : 6-trichloro-3-nitro-acid do not show any similar relationship. E. W. W.

Chlorination of Benzoic Acid. WILHELM LOSSEN (D.R.-P. 146174).—In the chlorination of benzoic acid by ordinary methods, the *meta*-isomeride is almost exclusively obtained. The *ortho*- and *para*-isomerides may be obtained by acting on benzoic acid with a dilute solution of a hypochlorite or with molecular proportions of alkali hydroxide and chlorine at a temperature not exceeding 50°. The chlorobenzoic acids formed are separated by fractional precipitation with dilute hydrochloric acid. The *meta*- and *para*-acids separate first, *o*-chlorobenzoic acid being obtained in a pure state from the last fraction. C. H. D.

Preparation of *N*-Arylanthranilic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145189).—The halogen atom of *o*-halogenbenzoic acids reacts with aromatic bases in presence of copper powder or copper salts (compare this vol., i, 50). Thus, phenylanthranilic acid is prepared by heating potassium *o*-chlorobenzoate with aniline, copper powder, and water. o-*Tolylanthranilic acid*, from *o*-toluidine, crystallises in silvery leaflets and melts at 188—189°; p-*tolylanthranilic acid* is similar, and melts at 191—192°. *a-Naphthylanthranilic acid* crystallises from alcohol in needles melting at 205—206°, insoluble in water. *β-Naphthylanthranilic acid* melts at 208—209°. C. H. D.

Preparation of Anthranilic Acid from Sulphoanthranilic Acid. KALLE & Co. (D.R.-P. 146716).—The sulpho-group may be removed from sulphoanthranilic acid by electrolytic reduction in neutral or slightly acid solutions, a mercury cathode and a current-density of 100—1000 amperes per sq. metre being employed.

C. H. D.

History of Anthranil. Gustav Heller (*Ber.*, 1903, 36, 4178—4188. Compare Abstr., 1895, i, 524; 1902, i, 779).—Mainly a polemical reply to Bamberger (Abstr., 1903, i, 432). In support of the formula $C_6H_4<\overset{CO}{\underset{NH}{|}}$ for anthranil, the following additional facts are brought forward (compare also Heller, Abstr., 1903, i, 827). The phenylhydrazone of *o*-aminobenzaldehyde is formed by the action of phenylhydrazine on anthranil at the ordinary temperature.

Stannic chloride and a solution of anthranil in concentrated hydrochloric acid yield a crystalline precipitate of $(C_7H_5ON)_2,H_2SnCl_6$. It turns red at 195°, decomposes at 243°, and is hydrolysed by dilute hydrochloric acid.

Anthranil and benzenesulphonic chloride at 150° yield a *compound*, $C_{20}H_{14}O_4N_2S$, *benzenesulphodianthranil*, which crystallises from benzene in minute needles melting at 211—212°.

When methylated with methyl sulphate at the ordinary temperature, anthranil yields the pure *N*-methyl ether, $C_6H_4<\overset{CO}{\underset{NMe}{|}}$, in the form of an oil, which distils at 245° with slight decomposition, or at 162° (corr.) under 40 mm. pressure. Its *salts* are readily soluble, but sparingly soluble double salts with stannic chloride and mercuric chloride have been obtained. The *ferricyanide* forms dark-coloured crystals, the *thiocyanate* colourless crystals, the *platinichloride* pale yellow aggregates melting and decomposing at 199—200°, and the *aurichloride* needles melting at 125—127°.

Methylanthranil and phenylhydrazine at the ordinary temperature yield the *phenylhydrazone* of *o*-methylaminobenzaldehyde in the form of long, yellow needles melting at 123—124°. When heated with dilute alkali hydroxides at 150°, the methyl ether yields methylanthranilic acid and methylaniline. J. J. S.

Optical Behaviour and Constitution of Nitrosoalkylurethanes and Anthranil. A Correction. Julius W. Brühl (*Ber.*, 1903, 36, 4294—4295).—Certain of the values given by the author and quoted in a previous abstract (this vol., i, 92) have been found to be erroneous. The corrected values are as follows. Nitrosoethylurethane, n_D 1·43676; $\mathfrak{M}_D$ 35·12. Nitrosomethylurethane, n_D 1·43905; $\mathfrak{M}_D$ 30·45. Anthranil, n_D 1·58452; $\mathfrak{M}_D$ 33·70. Methylanthranil, n_D 1·57795; $\mathfrak{M}_D$ 38·94. A. McK.

Unsaturated Compounds. I. Action of Hydroxylamine on Unsaturated Acids. Theodor Posner (*Ber.*, 1903, 36, 4305—4318).—The different unsaturated acids were caused to interact with freshly prepared free hydroxylamine in alcoholic solution, either at the ordinary temperature or at the boiling point. *a-Hydroxylamino-β-phenylpropionic acid*, $CH_2Ph\cdot CH(NH\cdot OH)\cdot CO_2H$, obtained from cinnamic acid, separates from alcohol as a white, lustrous, crystalline powder and melts and decomposes at 165°. When reduced, it gives phenylalanine (*infra*), and on oxidation with ammoniacal silver nitrate is converted into a *compound*, $C_9H_7O_2N$, which crystallises from benzene in colourless, silky needles melting at 148—150°. When ethyl cinnamate interacts with hydroxylamine solution at the ordinary

temperature, a colourless *compound* is formed which, after two crystallisations from alcohol, melts at 114—115°, and on further crystallisation undergoes decomposition; analyses point to the formula $C_7H_{12}N_2O_3$, although this is improbable, because the substance is easily oxidised by ammoniacal silver nitrate to the foregoing compound, $C_9H_7O_2N$. Moreover, when warmed with water, it evolves carbon dioxide and nitrogen, and is converted, with an excellent yield, into phenylalanine (α-amino-β-phenylpropionic acid), which melts at 231°, not at 261° as stated by Erlenmeyer and Lipp (Abstr., 1882, 971); it was characterised by its copper salt and benzoyl derivative. On replacing the amino-group of phenylalanine by the hydroxyl radicle, *β-phenyl-α-lactic acid*, $CH_2Ph\cdot CH(OH)\cdot CO_2H$, is obtained, which crystallises from chloroform and melts at 96°.

*α-Hydroxylamino-β-phenyl*iso*butyric acid*,

$$CH_2Ph\cdot CMe(NH\cdot OH)\cdot CO_2H,$$

obtained from α-methylcinnamic acid, forms nacreous leaflets, and on recrystallisation is partly decomposed; it readily loses hydroxylamine and regenerates α-methylcinnamic acid, and on this account cannot be reduced to the corresponding amino-derivative. From ethyl α-methylcinnamate and hydroxylamine, a crystalline *compound* melting at 119° is obtained of undetermined constitution; it undergoes decomposition when recrystallised.

α-Hydroxylamino-α-phenylpropionic acid, $OH\cdot NH\cdot CMePh\cdot CO_2H$, prepared from atropic acid and hydroxylamine, could only be obtained as a syrup; when boiled with an excess of alcoholic hydroxylamine, it is reduced to *α-amino-α-phenylpropionic acid*, which is best prepared by heating atropic acid directly with an excess of the base, and melts after crystallisation from water at 233°; the amino-acid is easily converted into atrolactic acid (α-hydroxy-α-phenylpropionic acid).

γ-(or β-)*Hydroxylamino-γ-phenyl*-n-*butyric acid*,

$$OH\cdot NH\cdot CHPh\cdot CH_2\cdot CH_2\cdot CO_2H$$

or $CH_2Ph\cdot CH(NH\cdot OH)\cdot CH_2\cdot CO_2H$, prepared from *iso*phenylcrotonic acid, crystallises from chloroform in lustrous leaflets, melts at 108°, and so readily loses hydroxylamine that it cannot be converted into the corresponding amino-compound.

α-Hydroxylaminobutyric acid, $CH_3\cdot CH_2\cdot CH(NH\cdot OH)\cdot CO_2H$, obtained from crotonic acid, crystallises from alcohol and melts at 144°; the corresponding α-aminobutyric acid could not be obtained pure.

Fumaric and maleic acids do not interact additively with hydroxylamine, but give rise only to their hydroxylamine salts. W. A. D.

Chemical Action of Light. VII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1903, **36**, 4266—4272. Compare Abstr., 1903, i, 562).—In their fifth communication on this subject (Abstr., 1903, i, 171), the authors examined the action of light on unsaturated compounds. Further details are now given.

The polymerisation of cinnamic acid to α-truxillic acid takes place only with the solid acid. The conversion of coumarin into dihydrocoumarin, on the other hand, occurs both with solid coumarin and with its solutions. When stilbene was exposed to light in a desiccator in the presence of air, a sublimate of benzoic acid was obtained. In accordance with Engler's views on autoxidation, the stilbene may

be regarded as forming a peroxide which suffers decomposition into benzaldehyde; the latter, then, under the influence of light is partly resinified and partly oxidised.

Maleic acid, both solid and in aqueous solution, is very slowly converted into fumaric acid in the absence of a catalyst such as bromine or iodine.

In an analogous manner to the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid studied by the authors, *o*-nitrobenzylideneaniline is converted into *o*-nitrosobenzanilide (Sachs and Kempf, Abstr., 1902, i, 682). On those grounds, it was expected that nitrobenzaldoxime would undergo rearrangement, thus:

$$NO_2\cdot C_6H_4\cdot CH{:}N\cdot OH \longrightarrow NO\cdot C_6H_4\cdot CO\cdot NH\cdot OH;$$

it was found, however, that the *anti*-oxime was transformed into the *syn*-oxime, $\begin{matrix} NO_2\cdot C_6H_4\cdot C\cdot H \\ \quad\quad\quad OH\cdot N \end{matrix} \longrightarrow \begin{matrix} NO_2\cdot C_6H_4\cdot C\cdot H \\ \quad\quad\quad N\cdot OH \end{matrix}$, the nitro-grouping taking no part in the action. The transformation is that of the maleinoid into the fumaroid type, and is an interesting instance of a confirmation of the stereochemical theory of the isomerism of oximes.

anti-*o*-Nitrobenzaldoxime, melting at 102—103°, was converted into *syn* *o*-nitrobenzaldoxime, melting at 148—150°. *anti*-*p*-Nitrobenzaldoxime, melting at 128·5—129°, was converted into *syn*-*p*-nitrobenzaldoxime, melting at 174°, the conversion in this case taking place more readily than with the *o*-compound. On the other hand, *m*-nitrobenzaldoxime, melting at 121°, suffered no transformation. Benzene was the solvent used in each case.

It is suggested that the *m*-oxime, melting at 121°, prepared from *m*-nitrobenzaldehyde, is the stable *syn*-oxime. The *anti*-oxime, prepared by the Beckmann method, is the unstable maleinoid form, which is converted by light into the stable *syn*-form.

The esterification of opianic acid by ethyl alcohol takes place in the absence of light (compare Abstr., 1903, i, 563), but not so quickly as in sunlight. A. McK.

Preparation of Aromatic Thio-acids and their Amides. Celso Ulpiani and U. Ciancarelli (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 219—228).—*Trithiodiphenylacetic acid*,

$$CO_2H\cdot CHPh\cdot S\cdot S\cdot S\cdot CHPh\cdot CO_2H,$$

prepared by passing hydrogen sulphide (3 mols.) into a 10 per cent. solution of benzoylformic acid (2 mols.), forms white, triangular prisms, terminated at both ends by pyramids with slightly rounded angles, melting at 145—148°. With zinc and hydrochloric acid, it yields phenylacetic acid and hydrogen sulphide; bromine oxidises it to benzoic acid.

Thiolphenylacetic acid, $SH\cdot CHPh\cdot CO_2H$, obtained in the form of its potassium salt by the action of potassium hydroxide on trithiophenylacetic acid, is an oil slightly soluble in water and readily so in alcohol or ether; it reduces ferric chloride to the ferrous compound yielding a blue solution, whilst with excess of the ferric salt it gives a flocculent, yellow precipitate.

Dithiophenylacetic acid, $CO_2H\cdot CHPh\cdot S\cdot S\cdot CHPh\cdot CO_2H$, separated from the blue solution yielded by the action of ferric chloride on thiolphenylacetic acid, is deposited from ether in crystals melting at

198—200°; when treated with zinc and hydrochloric acid, it gives thiophenylacetic acid.

Trithiodiphenylacetamide, $S_3(CHPh\cdot CO\cdot NH_2)_2$, prepared by the action of hydrogen sulphide on benzoylformamide, crystallises from alcohol, with $1H_2O$, in microscopic, fragile aggregates of three rhombic prisms terminated by pyramids; when heated, it becomes red and melts at 217°; it is slightly soluble in acetone, ethyl acetate, light petroleum, chloroform, or carbon disulphide; potassium hydroxide hydrolyses it to thiolphenylacetic acid. T. H. P.

Chlorides of *p*-Bromo-*o*-sulphobenzoic Acid and some of their Derivatives. William M. Blanchard (*Amer. Chem. J.*, 1903, 30, 485—517).—The symmetrical *chloride* of *p*-bromo-*o*-sulphobenzoic acid, $COCl\cdot C_6H_3Br\cdot SO_2Cl$, melts at 99—100°, whilst the unsymmetrical *chloride*, $C_6H_3Br<\substack{CCl_2\\SO_2}>O$, melts at 89—90°.

When the symmetrical chloride is treated with ammonia, it is converted into *p*-bromobenzoicsulphinide. By the action of ammonia on the unsymmetrical chloride, *p*-bromobenzoicsulphinide and ammonium *p*-bromo-*o*-cyanobenzenesulphonate are produced, the proportion of the former decreasing with dilution of the ammonia, being 26 per cent. with concentrated ammonia, 15 per cent. with dilute ammonia (1 : 3), and 6 per cent. with very dilute ammonia (1 : 20).

By the action of aniline on the symmetrical chloride at the ordinary temperature, a mixture of the anil and symmetrical anilide is produced. The *anil* of *p*-bromo-*o*-sulphobenzoic acid,

$$C_6H_3Br<\substack{CO-\\SO_2}>NPh,$$

crystallises from alcohol in long, slender needles or narrow, thin plates, melts at 184·5°, and is readily soluble in benzene, chloroform, acetone, or glacial acetic acid. If the anil is heated with boiling aniline for $1\frac{1}{2}$ hours, it is converted into the symmetrical anilide. The symmetrical *anilide*, $NHPh\cdot CO\cdot C_6H_3Br\cdot SO_2\cdot NHPh$, forms short, silky needles, melts at 236—239°, and is easily soluble in chloroform, acetone, benzene, or glacial acetic acid. When the unsymmetrical chloride is treated with aniline, a mixture of the symmetrical and unsymmetrical anilides is obtained. The unsymmetrical *anilide*, $C_6H_3Br<\substack{C(NHPh)_2\\SO_2}>O$, crystallises in short needles, does not melt below 300°, and is only slightly soluble in the usual organic solvents.

The *dianil* of *p*-bromo-*o*-sulphobenzoic acid,

$$C_6H_3Br<\substack{C(NPh)\\SO_2}>NPh,$$

obtained by the action of phosphorus oxychloride or phosphoric oxide on either the symmetrical or the unsymmetrical anilide, crystallises from glacial acetic acid in small, bright yellow plates, melts at 199—200°, and is readily soluble in alcohol, benzene, or chloroform. If a solution of the dianil in glacial acetic acid or alcoholic potassium hydroxide is boiled for some time, the unsymmetrical anilide is produced. When the dianil is heated with concentrated hydrochloric acid, it is converted into the anil.

The symmetrical chloride undergoes no change when heated with

phosphorus oxychloride at 130° in a sealed tube, and neither chloride is appreciably decomposed when kept at 100° in a sealed tube for several days.

p-*Bromo*-o-*cyanobenzenesulphonic acid*, $CN\cdot C_6H_3Br\cdot SO_3H$, is very soluble in water. When an aqueous solution of this acid is boiled for 5 hours with dilute hydrochloric acid, it remains unchanged, but when boiled for 5 hours with dilute sodium hydroxide or potassium hydroxide, the sodium or potassium *p*-bromo-*o*-carbaminebenzenesulphonate is produced, and if the boiling is continued for 10 hours longer, the corresponding *p*-bromo-*o*-sulphobenzoate is formed. *Ammonium*, *potassium*, *sodium*, *barium*, *magnesium*, and *copper* *p*-bromo-*o*-cyanobenzenesulphonates are described.

p-Bromo-*o*-carbaminebenzenesulphonic acid, $NH_2\cdot CO\cdot C_6H_3Br\cdot SO_3H$, was not obtained in a free state, but its *sodium* and *potassium* salts are described. When these salts are boiled for 10 hours with dilute sodium hydroxide or potassium hydroxide, they are partly converted into the corresponding *p*-bromo-*o*-sulphobenzoates.

p-*Bromo*-o-*sulphaminebenzoic acid*, $CO_2H\cdot C_6H_3Br\cdot SO_2\cdot NH_2$, obtained by heating *p*-bromobenzoicsulphinide with potassium hydroxide for 5 hours, crystallises in long, thin, lustrous plates, melts at 192—197°, and is readily soluble in hot water, but only slightly so in cold water. When heated at 160°, it suffers decomposition with formation of *p*-bromobenzoicsulphinide and ammonium *p*-bromo-*o*-sulphobenzoate. If the acid is heated with dilute hydrochloric acid, it is rapidly converted into ammonium hydrogen *p*-bromo-*o*-sulphobenzoate,

$$CO_2H\cdot C_6H_3Br\cdot SO_3\cdot NH_4,$$

but if heated with dilute alkali hydroxide, this hydrolysis does not take place, even if the heating is continued for 10 hours. *p*-Bromo-*o*-sulphaminebenzoic acid may be prepared also by boiling *p*-bromobenzoicsulphinide with dilute hydrochloric acid for 45 minutes, but if the heating is continued for a longer time, ammonium hydrogen *p*-bromo-*o*-sulphobenzoate is produced. The salts of this acid are more soluble in water than the acid itself, and when heated above 150° are converted into the corresponding salts of *p*-bromobenzoicsulphinide. The *calcium*, *strontium*, *barium*, *sodium*, *potassium*, *magnesium*, and *copper* salts are described.

When *p*-bromobenzoicsulphinide is heated with phosphorus pentachloride in a sealed tube, *p*-bromo-*o*-cyanobenzenesulphonic chloride and *p*-bromo-*o*-chlorobenzonitrile are produced. If the temperature is not allowed to rise above 150°, the sulphonic chloride is the chief product, but if the temperature is raised to 200°, the larger proportion of the product consists of *p*-bromo-*o*-chlorobenzonitrile.

p-*Bromo*-o-*cyanobenzenesulphonic chloride*, $CN\cdot C_6H_3Br\cdot SO_2Cl$, crystallises in white plates, melts at 82°, and is readily soluble in benzene, glacial acetic acid, or hot light petroleum. When boiled with water, it is converted into *p*-bromo-*o*-cyanobenzenesulphonic acid, and if heated with sulphuric acid, it is converted into *p*-bromo-*o*-sulphobenzoic acid.

p-*Bromo*-o-*chlorobenzonitrile*, $C_6H_3BrCl\cdot CN$, is volatile with steam, crystallises in white needles, melts at 51—61°, is very soluble in benzene, glacial acetic acid, or light petroleum, and when heated with hydrochloric or sulphuric acid is converted into *p*-bromo-*o*-chlorobenzoic acid. E. G.

Physiological Relationships of Proteids containing Sulphur. III. Constitution of Mercapturic Acids. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1903, 4, 486—510. Compare Abstr., 1902, i, 731; 1903, i, 75, 301; Baumann and Preusse, Abstr., 1882, 756; König, Abstr., 1892, 1090; Weiss, Abstr., 1895, i, 284; Fränkel, *ibid.*).—Baumann's *p*-bromophenylcystein or α-amino-α-*p*-bromophenylthiolpropionic acid, on treatment with nitrous acid by Jochem's method (Abstr., 1901, i, 129), yields (1) *α-hydroxy-α-p-bromophenylsulphonpropionic acid*, $C_6H_4Br\cdot SO_2\cdot CMe(OH)\cdot CO_2H$, melting at 149° and soluble in ether; (2) *α-chloro-α-p-bromophenylthiolpropionic acid*, $C_6H_4Br\cdot S\cdot CMeCl\cdot CO_2H$, as an oil which on treatment with alkali yields hydrochloric acid and bromophenylmercaptan; (3) *α-amino-α-p-bromophenylsulphonpropionic acid*, $C_6H_4Br\cdot SO_2\cdot CMe(NH_2)\cdot CO_2H$, crystallising in needles and melting and decomposing at 196° (compare König); and (4) a compound melting at 192° and probably an α-amino-α-*p*-bromophenylthiolpropionic acid. A better yield of the chloro-acid may be obtained by a slightly modified process, and on reduction with tin and hydrochloric acid it yields a small amount of α-*p*-bromophenylthiolpropionic acid, melting at 115—116° and yielding a characteristic cherry-red coloration with concentrated sulphuric acid.

The ethyl ester of the α-chloro-α-bromophenylthiolpropionic acid, on reduction with water and aluminium amalgam, yields an ester which on hydrolysis gives the same bromophenylthiolactic acid, melting at 115—116°. In order to determine the position of the $S\cdot C_6H_4Br$ group, the bromphenyl-α- and β-thiolactic acids have been synthesised; the β-acid, $C_6H_4Br\cdot S\cdot CH_2\cdot CH_2\cdot CO_2H$, is in all respects identical with the acid melting at 115—116°.

p-Bromophenyldiazonium chloride and potassium xanthate react, yielding an explosive additive compound, but if this is carefully decomposed by warm water, ethyl *p*-bromophenylxanthate is obtained as an oil, and on hydrolysis it yields an 87 per cent. yield of *p*-bromophenylmercaptan.

p-Bromophenyl-α-thiolactic acid, $C_6H_4Br\cdot S\cdot CHMe\cdot CO_2H$, obtained by the action of α-bromopropionic acid on the mercaptan, forms rhombic plates, sinters at 107°, melts at 112°, and gives no characteristic coloration with concentrated sulphuric acid.

p-Bromophenyl-β-thiolactic acid may be obtained by the action of bromophenylmercaptan on β-iodopropionic acid in the presence of alkali, or of *p*-bromophenyldiazonium chloride on β-thiolactic acid, and is in all respects identical with the acid melting at 115—116°.

The mercapturic acids are therefore not αα-substituted propionic acids, as suggested by Baumann, and the pyruvic acid obtained by hydrolysis is presumably formed by secondary reactions. *p*-Bromophenylcystein is thus $C_6H_4Br\cdot S\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, and the *p*-bromophenylmercapturic acid, $C_6H_4Br\cdot S\cdot CH_2\cdot CH(NHAc)\cdot CO_2H$. The relationship between the mercapturic acid and proteid cystein is thus extremely simple. Cystein hydrochloride forms a relatively stable additive compound with *p*-bromophenyldiazonium chloride, which on treatment with dilute sodium carbonate solution yields *p*-bromophenylcystein (16 per cent.), melting at 181°, but this, when warmed for a short time with dilute mineral acids, yields an isomeric compound

melting at 192—193° (compare Baumann). *p*-Bromophenylcystein may be converted into *p*-bromophenylmercapturic acid, melting at 152—153°, when acetylated with acetyl chloride in the presence of pyridin. The complete synthesis of mercapturic acid from cystein has thus been accomplished.

The *p*-bromophenylcystein melting at 192—193° yields an *acetyl* derivative, melting at 153—154° but not identical with bromophenylmercapturic acid. J. J. S.

Some Compounds of Bismuth with the Hydroxybenzoic Acids. PAUL THIBAULT (*Bull. Soc. chim.*, 1904, [iii], 31, 36—38).—*Bismuth* p-*hydroxybenzoate*, $(C_7H_5O_3)_3Bi$, forms colourless, transparent needles, and is easily decomposed by water. *Bismuthyl β-resorcylate*, $C_6H_3(OH)_2O\cdot BiO$, crystallises in transparent needles of sp. gr. 2·62 at 16°, insoluble in water and all ordinary solvents. *Bismuthyl* 2 : 5-*dihydroxybenzoate*, $C_6H_3(OH)_2\cdot O\cdot BiO$, is obtained as pale yellow, transparent needles, which are insoluble in water. S. S.

Constitution of Aromatic Purpuric Acids. IV. Synthesis of 3 : 5-Dinitro-4-cyano-2-hydroxytoluene. WALTHER BORSCHE and E. BÖCKER (*Ber.*, 1903, 36, 4357—4361. Compare Abstr., 1900, i, 645; 1902, i, 226).—The purpuric acids, prepared by the action of potassium cyanide on polynitrophenols, are oxidised to polynitrohydroxynitriles. Thus the purpurate from dinitro-*o*-cresol yields a 3 : 5-dinitrocyano-2-hydroxytoluene, in which the cyano-group occupies either the 4- or 6-position. The 4-cyano-compound has been prepared, and is found to be identical with the product from the purpuric acid. In the action of potassium cyanide on dinitro-*o*-cresol, it is therefore the hydrogen atom between the two nitro-groups which is replaced by the cyano-group.

4-Cyano-2-hydroxytoluene, $CN\cdot C_6H_3Me\cdot OH$, prepared by boiling the diazonium sulphate from 4-cyano-*o*-toluidine with water, crystallises from dilute alcohol in white needles and melts at 99·5°. Nitric acid of sp. gr. 1·49 converts it into 3 : 5-dinitro-4-cyano-2-hydroxytoluene, crystallising from dilute nitric acid in long, yellow needles and melting at 148°, identical with the product from *o*-cresolpurpuric acid. When the action of the nitric acid is interrupted after a few minutes, two mononitro-derivatives may be obtained and separated by fractional crystallisation from dilute alcohol; they then melt at 141—142° and 191—193°. 3 : 5-*Dinitro-2-hydroxy-4-toluic acid* could not be prepared from the nitrile, but is obtained by the nitration of 2-hydroxy-4-toluic acid, and crystallises from alcohol in bright yellow leaflets melting at 200°. C. H. D.

Organo-magnesium Derivatives of Monobromophenolic Ethers: Action of Carbon Dioxide. F. BODROUX (*Bull. Soc. chim.*, 1904, [iii], 31, 30—33).—Compounds of the type $OR\cdot C_6H_4\cdot MgBr$ may be prepared by the action of magnesium on brominated phenolic ethers. Carbon dioxide decomposes these organo-magnesium bromides with formation of the corresponding acids, $OR\cdot C_6H_4\cdot CO_2H$. In this

way, anisic acid and *p*-ethoxybenzoic acid were synthesised. The same reaction was carried out on the naphthalene series and led to the synthesis of 2-methoxy-α-naphthoic acid, *2-ethoxy-α-naphthoic acid*, which forms colourless plates soluble in alcohol melting at 142°, and *2-propoxy-α-naphthoic acid*, which crystallises in radiating groups of colourless needles melting at 79°. S. S.

Preparation of Indoxyl from Formylmethylanthranilic Acid. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 145601).—Methylanthranilic acid is converted into indoxyl by fusion with alkali (D.R.-P. 79409). Formylmethylanthranilic acid, prepared by oxidation of quinoline methyl haloids, is more readily obtainable in quantity than the methyl acid, and is converted into indoxyl by fusion of its alkali salts with sodamide. The action is violent, and should be moderated by adding alkali hydroxides or cyanides to the fused mixture. The cooled mass dissolves in water and rapidly absorbs oxygen from the air, forming indigotin. C. H. D.

Preparation of Bromoindigotin. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 145910).—The preparation of bromoindigotin by the action of bromine on indigo-white (this vol., i, 57) may be modified by employing the sodium salt of indigo-white, or indigo-white itself in presence of acids or metallic salts. The yield is increased by such additions. C. H. D.

Products of the Condensation of Ethyl Benzoylacetate with Benzaldehyde. Corrado Bertini (*Gazzetta*, 1903, 33, ii, 145—152).—By the action of benzaldehyde (3 mols.) on ethyl diazoacetate (2 mols.), Buchner and Curtius (Abstr., 1885, 1238) obtained an ethyl benzylidenebisbenzoylacetate melting at 103°, whilst the compound of the same structure prepared by Knoevenagel (Abstr., 1895, i, 48) by condensing ethyl benzoylacetate with benzaldehyde in presence of diethylamine, melted at 95°. The author shows that this ester exists in tautomeric forms.

For the preparation of the ester, a mixture of an aqueous alcoholic solution of ethyl benzoylacetate (2 mols.), benzaldehyde (1 mol.), and a little piperidine was heated for an hour. The products were (1) ethyl benzylidenebenzoylacetate, which yields a *dibromo*-derivative,

$$CHPhBr\cdot CBzBr\cdot CO_2Et,$$

separating from alcohol in long, shining needles melting at 110°. (2) Crystals, which, when deposited from benzene, melt and decompose at 95°, and in alcoholic solution give an intense coloration with ferric chloride; this is probably the enolic form of ethyl benzylidenebisbenzoylacetate. (3) Two other modifications of ethyl benzylidenebisbenzoylacetate, neither of which gives a coloration with ferric chloride. The first separates from alcohol in small needles melting at 132°, and has the normal molecular weight in boiling benzene; the second melts at 93—94°, but gives abnormal values for the molecular weight in boiling benzene, owing to partial decomposition into ethyl benzylidenebenzoylacetate.

n 2

Attempts were made to obtain larger quantities of the enolic (?) ester, melting at 95°, by treating the mixture of esters (3) in alcoholic solution with sodium, but the product obtained was *dehydrobenzylidenebisbenzoylacetic acid*, $CHPh<\begin{matrix}C(CO_2H):CPh\\C(CO_2H):CPh\end{matrix}>O$, which crystallises from aqueous alcohol in shining, nacreous scales melting and decomposing at 141°; it has the normal molecular weight in boiling benzene, and gives no coloration with ferric chloride. The *sodium*, *copper*, and *silver* salts were prepared. T. H. P.

o-**Fluorenoylbenzoic Acid and its Isomeric Methyl Esters.** GUIDO GOLDSCHMIEDT and ALFRED LIPSCHITZ (*Ber.*, 1903, **37**, 4034—4039).—o-*Fluorenoylbenzoic acid*, $\begin{matrix}C_6H_4\\|\\CH_2\end{matrix}>C_6H_3\cdot CO\cdot C_6H_4\cdot CO_2H$, prepared by the action of phthalic anhydride on fluorene in light petroleum solution in presence of aluminium chloride, crystallises from dilute methyl alcohol or glacial acetic acid in microscopic, white needles, and melts at 227—230° after sintering at 220°. Even in traces, it produces an intense reddish-violet coloration in concentrated sulphuric acid. It is a carboxylic acid of Fortner's benzoylfluorene (Abstr., 1903, i, 177), but could not be converted into the ketone by distillation with lime, although distillation with zinc dust gave benzylfluorene.

The *methyl* ester, $C_{22}H_{16}O_3$, prepared by the action of methyl alcohol and sulphuric acid on the acid or of methyl iodide on the silver salt, crystallises from methyl alcohol in microscopic prisms and melts at 126—128°. The chloride of the acid, prepared by means of thionyl chloride, reacts with methyl alcohol, forming the same ester, and also thin, rectangular leaflets of an isomeride melting at 200—202°. The more fusible ester is less readily hydrolysed by potassium hydroxide than the other. The compound melting at 200—202° must be regarded as the ψ-ester, and that melting at 126—128° as the true ester, in accordance with the method of preparation and with the general rule that the ψ-esters of the similarly constituted *o*-aldehydo-acids have higher melting points and are more readily hydrolysed than the true esters. C. H. D.

Preparation of Diphenylamine-2 : 2′-dicarboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 145605).—In the preparation of anthranilic acid (see this vol., i, 50), *diphenylamine-2 : 2′-dicarboxylic acid* is obtained as a by-product, the proportion being greater when the reaction is carried out under pressure. The acid forms a colourless, crystalline powder melting and decomposing at about 300°, and dissolving very sparingly in water or organic solvents. The *sodium* salt is sparingly soluble in dilute sodium hydroxide. C. H. D.

Fluorescence of Naphthalic Anhydride and some of its Derivatives. LUIGI FRANCESCONI and G. BARGELLINI (*Gazzetta*, 1903, **33**, ii, 129—133. Compare Abstr., 1903, i, 34).—The modifications

made by Hewitt (Abstr., 1903, i, 346) in his theory of fluorescence does not bring this into accord with the facts that naphthalic anhydride fluoresces whilst phthalic anhydride does not. According to R. Meyer's theory (Abstr., 1898, ii, 105 and 275), the latter anhydride contains no fluorophore ring, but both naphthalic anhydride and naphthalimide contain the pyrone ring, which, according to this author, is one of the fluorophore groupings.

The manner in which the members of the fluorophore ring are combined is apparently without influence on the fluorescence. Thus acenaphtheneimine exhibits fluorescence, as also, although in feebler degree, do the mono- and di-oximes and the monohydrazone of acenaphthenequinone; in the latter compounds, the fluorescence increases either on long keeping or on heating, possibly on account of molecular rearrangement, for example, of the mono-oxime of acenaphthenequinone into naphthalimide.

Meyer's theory may be widened in its scope. As the introduction of one of the electro-negative groups, OH, Cl, Br, I, NO_2, diminishes the fluorescence, it may possibly be assumed that electro-positive groups, such as NH_2 and NMe_2, are capable of converting simpler groups into fluorophores.

Like colour, fluorescence depends on two factors: the presence of a special fluorophore group and the nature and position of substituting residues. Thus, most amino-compounds show a far more intense fluorescence than the corresponding hydroxyl derivatives.

T. H. P.

Parasantonide and Parasantonic Acid. I, II, and III. Luigi Francesconi (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 204—208, 267—273, 304—311).—Parasantonide, which was prepared by Cannizzaro and Valente by boiling santonic acid for a long time with glacial acetic acid, distilling off the latter, and heating the residue at 260—300°, may be obtained more easily and in better yield by substituting metasantonic for santonic acid. It separates from the ordinary solvents in rhombic crystals melting at 110°, has the normal molecular weight in freezing acetic acid or boiling alcohol, and in chloroform solution has $[\alpha]_D$ +891·7°. It must be regarded as the lactone of parasantonic acid, which it yields under the action of an alkali hydroxide or hydrochloric acid, whilst also parasantonic acid is re-converted into parasantonide by means of acetic anhydride.

If, in the above-described method of preparation of parasantonide, the heating of the residue be limited to 180°, santonide, stereoisomeric with parasantonide, is obtained; this substance has $[\alpha]_D$ +744·61° and, with an alkali hydroxide or hydrochloric acid, yields *iso*santonic acid, which melts at 152°, has $[\alpha]_D$ −73·92° in chloroform solution, and forms methyl and ethyl esters melting at 69—70° and 76° respectively; the former has $[\alpha]_D$ −50·2°. With acetic anhydride, *iso*santonic acid yields santonide.

Parasantoninimide, $C_{15}H_{19}O_2N$, obtained by saturating an alcoholic solution of parasantonide with gaseous ammonia, separates from the mother liquor in hard, shining crystals, which dissolve readily in

alcohol or acetic acid and to a less extent in ether, and melt at 216—217°; it dissolves in concentrated hydrochloric acid, from which it crystallises unchanged, and also in boiling concentrated potassium hydroxide, which converts it into parasantonic acid with evolution of ammonia; in alcoholic solution, it has $[\alpha]_D$ +1135°. Its *acetyl* derivative, $C_{17}H_{21}O_3N$, crystallises from ether in shining needles melting at 169—170° and dissolving readily in acetic acid or alcohol; in alcoholic solution it has $[\alpha]_D$ +697·2°; when heated with alcoholic potassium hydroxide, it gives first the imide and then parasantonic acid.

In the cold, hydroxylamine and parasantonide interact, forming *parasantoninhydroxamic acid* (?), $C_{15}H_{21}O_4N$, which crystallises from aqueous alcohol in needles softening at 165° and melting at 180°; it dissolves readily in alcohol or ethyl acetate, and to a less extent in ether. When heated at 100°, it loses 1 mol. H_2O, forming *oximidoparasantonin* (?), $C_{15}H_{19}O_3N$, which in alcoholic solution has $[\alpha]_D$ +999·09°. The hydroxamic acid is stable to dilute hydrochloric acid and dissolves in cold solutions of alkaline hydroxides or carbonates, from which, even after prolonged heating, dilute acids precipitate it unchanged; its silver salt is white and blackens rapidly, even in the dark, with deposition of silver; with ferric chloride, its aqueous solution gives a transient violet coloration, which gives place to a white precipitate. By heating the hydroxamic acid or the oxime with acetic anhydride, an *anhydride*, $C_{30}H_{36}O_5N_2$, is obtained which crystallises from a mixture of acetic anhydride and ether in long, silky needles melting at 258°; slightly soluble in ethyl acetate, more so in alcohol, but insoluble in alkali carbonate solutions. The *monoacetyl* derivative of the oxime, obtained by adding sodium nitrite solution to a glacial acetic acid solution of the oxime, separates in needles which are soluble in alcohol or ethyl acetate and melt at 176°.

Hydroxyparasantoninimide (?), $C_{15}H_{19}O_3N$, obtained by heating the isomeric oximidoparasantonin with hydrochloric acid, is soluble in ethyl acetate or alcohol, from which it separates in shining, rhombic crystals melting at 256°; in alcohol, it has $[\alpha]_D$ +200·1°; it is stable to boiling water and crystallises unchanged from solutions of the alkali carbonates; it does not combine with acetic anhydride, hydroxylamine, or semicarbazide, is not reduced by zinc and acetic acid, and gives no nitroso-compound. When treated with alkali hydroxides, it gives up ammonia and forms *hydroxyparasantonic acid*, $C_{15}H_{20}O_5$, which dissolves readily in water, alcohol, or ethyl acetate and slightly in ether, and crystallises from alcohol in long, stout needles melting at 189—190°; in alcoholic solution, it has $[\alpha]_D$ +89·8°. Its *barium* salt is readily soluble in water. Its *methyl* ester dissolves readily in ether, alcohol, or ethyl acetate, from which it crystallises in long, stout needles melting at 138—139° and having $[\alpha]_D$ +36·4°; it does not combine with hydroxylamine or semicarbazide. The *monoacetyl* derivative, $C_{15}H_{19}O_4{\cdot}OAc$, separates from ethyl acetate in crystals, melts at 207°, dissolves in alcohol, and has $[\alpha]_D$ +64·3° in alcoholic solution; it is soluble in water and in solutions of alkali carbonates, from which it is deposited unchanged.

When heated, hydroxylamine and parasantonide (or parasantonin-

hydroxamic acid) yield a *compound*, $C_{15}H_{18}O_2N_2$, which separates from the ordinary solvents in prisms melting at 171—172°; it is moderately soluble in ethyl acetate or alcohol, and in the latter has $[\alpha]_D$ $-111{\cdot}9°$; it dissolves in acetic anhydride, which deposits it unchanged, and in alkali carbonate solutions.

Parasantonic acid, obtained by heating parasantonide with an alkali hydroxide solution or with concentrated hydrochloric acid, is soluble in alcohol, ethyl acetate, chloroform, or carbon tetrachloride, from all of which it separates in large, rhombic crystals melting at 170°; it has $[\alpha]_D$ $-98{\cdot}51°$ in chloroform solution; by the action on it of acetic anhydride, acetyl chloride, or phosphorus pentachloride, parasantonide is regenerated; it is an energetic acid, decomposing carbonates and being readily esterified in alcoholic solution by means of hydrogen chloride; its methyl ester melts at 183—184° and has $[\alpha]_D$ $-15°$, while the ethyl compound melts at 172° and has $[\alpha]_D$ $-99{\cdot}89°$.

With a solution of parasantonic acid in alkali hydroxide solution, hydroxylamine yields not an oxime, but a *compound*, $C_{15}H_{21}O_4N$, which crystallises from alcohol in shining, elongated prisms and cubiform polyhedra, and from ethyl acetate in crystals which are all cubiform; it melts and decomposes at 239—240° and has $[\alpha]_D$ $-92{\cdot}7°$. By heating with acetic anhydride, this compound gives up water, forming an *anhydride*, $C_{15}H_{19}O_3N$, which crystallises from ether in long, slender prisms melting at 171—172° and has $[\alpha]_D$ $+201{\cdot}7°$ in alcoholic solution; it dissolves in alkali hydroxide solution, being thereby transformed into the original compound melting at 239—240°.

Dibromoparasantonic acid, $C_{15}H_{18}O_4Br_2$, crystallises from a mixture of ether and light petroleum in mammillary masses of small prisms melting and decomposing at 176—177°; it dissolves readily in ethyl acetate or alcohol, and when treated with boiling water or with an alkaline hydroxide or carbonate it loses its bromine; in alcohol, it has $[\alpha]_D$ $+28{\cdot}0°$; reduction with zinc dust and hydrochloric acid yields parasantonic acid; saturation of the alcoholic solution with hydrogen bromide gas yields, as main product, the ethyl ester of a monobromo-acid (?), $C_{15}H_{21}O_4Br$.

Dihydroxyparasantonic acid, $C_{15}H_{20}O_6$, prepared by heating dibromoparasantonic acid with water or an alkali carbonate solution, forms shining, cubiform crystals which are readily soluble in alcohol or ethyl acetate and melt at 206—207°; it has $[\alpha]_D$ $-109{\cdot}7°$ in alcoholic solution. Its *barium* salt ($+H_2O$) is readily soluble in water.

Dehydrodihydroxyparasantonic acid, $C_{15}H_{18}O_5$, obtained by the action of an alkali hydroxide solution on dibromoparasantonic acid, separates from acetic acid in rosettes of needles and from water in microscopic, elongated prisms melting at 187—188°; it is soluble in ether or alcohol, and in the latter has $[\alpha]_D$ $-31{\cdot}55°$; its *barium* salt ($+H_2O$) which is readily soluble in water, and its *silver* salt were prepared; the *ethyl* ester is a syrupy compound. On oxidation with alkaline permanganate solution, the acid yields only oxalic acid, whilst when heated with sodium hydroxide at 250° it gives dihydroxyparasantonic acid. The chlorohydrin of *dehydrodihydroxyparasantonic acid*, $C_{15}H_{19}O_5Cl$, crystallises from alcohol in slender, shining needles which melt at 204—205° and dissolve easily in ethyl acetate, alcohol, or water; it has

$[\alpha]_D$ − 23·5° in alcoholic solution. The *chlorohydrin* of *ethyl dehydrodihydroxyparasantonate*, $C_{19}H_{27}O_5Cl$, crystallises from ethyl acetate in plates which have a fatty lustre and melt at 170—171°; it has $[\alpha]_D$ − 97·0° in alcoholic solution; it is readily hydrolysed by alkaline hydroxides, giving the chlorohydrin of the acid. The chlorohydrin of the methyl ester melts at 146° and that of the benzyl ester at 129—130°. T. H. P.

Kino: an Investigation of its Constituents. The Constitution of Kino-tannic Acid. EDMUND WHITE (*Pharm. J.*, 1903, [iv], 17, 702—704).—Numerous attempts were made to obtain kino-tannic acid in a crystalline form, but without success. When the acid was heated with acetic anhydride or acetyl chloride, amorphous products were obtained. On benzoylation by the Schotten-Baumann method or by means of benzoic anhydride, no crystalline product was formed. The *methyl* derivative of kino-tannic acid was obtained as amorphous, microscopic granules containing 29·25 per cent. of methoxyl. E. G.

A Supposed Oxime of Meconic Acid. ALBERTO PERATONER and A. TAMBURELLO (*Gazzetta*, 1903, 33, ii, 233—239).—The supposed oxime of meconic acid described by Odernheimer (Abstr., 1884, 1302) is really *hydroxylamine meconate*, $C_7H_4O_7,NH_2{\cdot}OH,H_2O$; this is shown by analysis and by the following facts. It interacts with piperonal giving meconic acid and piperonaldoxime, and is formed by the double decomposition of sodium meconate and hydroxylamine hydrochloride; it readily reduces Fehling's solution and ammoniacal silver nitrate, and its silver, calcium, and barium salts do not contain nitrogen, but are identical with the corresponding salts of meconic acid.

Calcium meconate, $C_7H_2O_7Ca,4H_2O$, is crystalline, and *barium meconate*, $C_7H_2O_7Ba,3H_2O$, amorphous. W. A. D.

Preparation of Aldehydes by the Aid of Organo-magnesium Compounds. LUDWIG GATTERMANN and F. MAFFEZZOLI (*Ber.*, 1903, 36, 4152—4153).—Aldehydes may be obtained by the action of ethyl formate (3 mols.) on organo-magnesium compounds (1 mol.). The following have been prepared: benzaldehyde, *o*- and *m*-tolualdehydes, anisaldehyde, phenylacetaldehyde, α-naphthaldehyde, and "camphoraldehyde" [hydroxymethylenecamphor]. The ester is dissolved in dry ether, cooled with solid carbon dioxide and ether to −50°, and to this the well-cooled ethereal solution of the magnesium compound is added. Ice-cold hydrochloric acid is then poured in and the mixture subjected to steam distillation after removal of the ether. J. J. S.

Reactions of Nitroxyl. ANGELO ANGELI and FRANCESCO ANGELICO (*Gazzetta*, 1903, 33, ii, 239—244. Compare Abstr., 1902, i, 78, 765; ii, 254).—Nitrohydroxylaminic acid is readily resolved into nitrous acid and nitroxyl, ⁚N·OH, which interacts additively with aldehydes, nitroso-compounds, and secondary amines.

On warming benzaldehyde with sodium nitrohydroxylaminate, benzhydroxamic acid, OH·CPh⁚N·OH, is obtained in nearly theoretical

quantity; similarly, from anisaldehyde and piperonaldehyde, the corresponding hydroxamic acids, $C_8H_9O_3N$ and $C_8H_7O_4N$, crystallising from acetone, are obtained.

From nitrosobenzene and from nitrosotoluene, the corresponding nitrosophenylhydroxylamine and nitroso-*p*-tolylhydroxylamine, of the type $R\cdot NO\colon N\cdot OH$ or $R\cdot N(NO)\cdot OH$, are obtained by the action of the nitrohydroxylaminic acid.

Piperidine hydrochloride gives with the sodium salt of the same acid the tetrazone, $C_5H_{10}N\cdot N\colon N\cdot C_5NH_{10}$, identical with Knorr's product from 1-aminopiperidine. Coniine gave an oil which was not analysed. W. A. D.

Dialdehydes prepared by the Action of Aldehydes on Aromatic Hydroxyaldehydes. III. *p*- and *m*-Nitrobenzylidenedivanillin Dimethyl Ethers. M. Rogoff (*Ber.*, 1903, 36, 3975—3978. Compare Abstr., 1902, i, 103, 547).—p-*Nitrobenzylidenedivanillin dimethyl ether*, $NO_2\cdot C_6H_4\cdot CH[C_6H_2(OMe)_2\cdot CHO]_2$, prepared by methylating the condensation product from nitrobenzaldehyde and vanillin, crystallises from dilute alcohol in microscopic prisms and melts at 186—188° (corr.). The *tetracetate*,

$$NO_2\cdot C_6H_4\cdot CH[C_6H_2(OMe)_2\cdot CH(OAc)_2]_2,$$

is precipitated from ethyl acetate by light petroleum in felted needles, and also melts at 186—188° (corr.).

m-*Nitrobenzylidenedivanillin dimethyl ether* crystallises from dilute alcohol in microscopic prisms and melts at 181—183° (corr.). The *bisphenylhydrazone*, $C_{37}H_{35}O_6N_5$, crystallises from acetic acid in microscopic needles and melts at 203·5—204·5° (corr.). T. M. L.

Conversion of Benzophenone into Triphenylcarbinol. Raymond Delange (*Bull. Soc. chim.*, 1903, [iii], 29, 1131—1132).—When benzophenone is heated with potash lime, it is converted into benzene and benzoic acid (Chancel, *Annalen*, 1849, 72, 279). The author finds that when heated with potassium hydroxide there is formed in addition a quantity of triphenylcarbinol (compare Haller and Minguin, Abstr., 1895, i, 601). The compound $OH\cdot CPh_2\cdot OK$ appears to be first formed; this, by direct fission, gives rise to benzene and benzoic acid, whilst by interaction between two mols. of this compound, triphenylcarbinol, benzoic acid, and water are produced. T. A. H.

Action of Hydroxylamine on Methenylbisindandione. Giorgio Errera (*Gazzetta*, 1903, 33, ii, 152—160).—If a mixture of methenylbisindandione (1 mol.), hydroxylamine hydrochloride (8 mols.), and 15 per cent. aqueous potassium hydroxide is heated for an hour on the water-bath, an interaction occurs according to the equation:

$$C_6H_4{<}{}^{CO}_{CO}{>}CH\cdot CH\colon C{<}{}^{CO}_{CO}{>}C_6H_4 + 9KOH + 4NH_3Cl\cdot OH =$$

$$2C_6H_4{<}{}^{C(NOK)}_{C(NOK)}{>}CH_2 + H\cdot CO_2K + 4KCl + 11H_2O,$$

the main product being the potassium derivative of indandionedioxime.

If, however, the heating is stopped immediately the ketone has dis-

solved, and the liquid still retains its dark red colour, and the solution then acidified with hydrochloric acid, the products obtained are: (1) indandionedioxime, (2) a substance insoluble in water, and (3) *hydroxylaminomethyleneindandione*, $C_6H_4<\substack{CO \\ CO}>C{:}CH\cdot NH\cdot OH$, which crystallises from alcohol in thin, orange needles melting at 250° when heated quickly; it dissolves slightly in water or benzene, and has acid properties, being readily soluble in solutions of ammonia, or potassium or sodium hydroxide, giving liquids which do not decompose on boiling; the addition of ferric chloride to the aqueous solution produces turbidity and a brownish-green colour, which disappears on acidifying; the *potassium* salt forms red, acicular crystals, and the *silver* salt a red precipitate.

The *anhydride* of *methenylbisindandionemonoxime*,

$$\begin{array}{l} CO\text{—}C{:}CH\text{–}C\cdot CO \\ \,| \qquad\quad | \qquad\quad || \;\; | \\ C_6H_4\cdot C{:}N\cdot O\cdot C\cdot C_6H_4 \end{array},$$

formed, together with indandionedioxime and hydroxylaminomethyleneindandione, by the interaction of hydroxylamine hydrochloride, an alcoholic solution of sodium, and methenylbisindandione, crystallises from acetic acid in orange-red needles, which melt and decompose at 303° when rapidly heated; it is soluble in xylene, and to a less extent in alcohol or benzene. It forms a *dioxime* (or *anhydride* of *methenylbisindandionetrioxime*), $C_{19}H_{11}O_3N$, which is obtained as a yellow powder melting and decomposing at about 312°; it is soluble to a slight extent in ordinary neutral solvents, and readily in solutions of bases; its *dibenzoyl* derivative, $C_{19}H_9ON(NOBz)_2$, crystallises from pyridine in minute, orange-red needles, which melt and decompose at about 280° when rapidly heated.

The *dibenzoyl* derivative of *a-diphenylenepyridinediketoxime*,

$$\begin{array}{l} OBz\cdot N{:}C\text{——}C{:}CH\cdot C\cdot C{:}NOBz \\ \qquad\quad | \qquad\; | \qquad\quad || \;\; | \\ \qquad\; C_6H_4\cdot C{:}N\text{—}C\cdot C_6H_4 \end{array},$$

separates from pyridine solution in needles melting and decomposing at about 250°. T. H. P.

Preparation of Chloranil. Otto N. Witt and Siegfried Toeche-Mittler (*Ber.*, 1903, 36, 4390—4392. Compare Graebe, Abstr., 1891, 1027).—A good yield of practically pure chloranil can be obtained by the following process. *p*-Nitroaniline is converted into 2 : 6-dichloro-4-nitroaniline, and this is reduced with tin and hydrochloric acid to 2 : 6-dichloro-*p*-phenylenediamine (*Ber.*, 1875, 8, 143). The pure compound need not be isolated, but the acid solution immediately chlorinated with potassium chlorate. J. J. S.

Action of Aniline on Tetrabromo-*o*-benzoquinone. C. Loring Jackson and Horace C. Porter (*Amer. Chem. J.*, 1903, 30, 518—537. Compare Jackson and Koch, Abstr., 1901, i, 597).—Hexabromo-*o*-dihydroxycatechol ether melts at 304—307° and crystallises from nitrobenzene in iridescent scales; its *monobenzoyl* derivative is a white, crystalline substance melting at 316—318°.

When hexabromo-*o*-quinocatechol ether is heated with hydrobromic acid at 100° in a sealed tube, it undergoes decomposition with forma-

tion of bromine, hexabromodihydroxycatechol ether, and a white, crystalline substance which is probably tetrabromocatechol.

When aniline is added to an alcoholic solution of tetrabromo-*o*-quinone, an additive *compound* of dianilinodibromo-*o*-quinone with aniline, $C_6Br_2O_2(NHPh)_2,NH_2Ph$, is first formed, which crystallises in pale brown needles and melts and decomposes at 121—124°. An additive *compound* with ethyl alcohol, $C_6Br_2O_2(NHPh)_2,EtOH$, is also obtained, which forms yellow plates and melts and decomposes at 142°; the corresponding *compound* with methyl alcohol melts and decomposes at 144—145°.

*Dianilinodibromo-*o*-quinone*, $C_6Br_2O_2(NHPh)_2$, prepared by repeatedly digesting its aniline compound with a mixture of benzene and light petroleum, crystallises in dark reddish-purple needles, melts at 160°, and is readily soluble in benzene, glacial acetic acid, or acetone.

If dianilinodibromo-*o*-quinone or one of its additive compounds is left with a mixture of aniline and alcohol or boiled for a few minutes with such a mixture, *dianilinobromo-*p*-quinoneanil*,

$$C_6HBrO(NHPh)_2{:}NPh,$$

is produced, which crystallises in brilliant, jet black plates, melts at 173°, and is freely soluble in benzene, glacial acetic acid, or acetone; this compound was first obtained by Zincke (Abstr., 1887, 808), but was not analysed by him. When dianilino-*p*-bromoquinoneanil is treated with an ethereal solution of sulphur dioxide, it is converted into dianilino-*p*-quinoneanil melting at 202—203°.

If dianilinodibromo-*o*-quinone is reduced by means of a dry ethereal solution of sulphur dioxide, a *substance* is produced which forms rosettes of small, green needles and melts at 186—188°; if, however, a moist ethereal solution is employed, other products are obtained which have not yet been completely examined.

When hexabromo-*o*-quinocatechol ether is treated with aniline, the same products are obtained as in the case of tetrabromo-*o*-quinone.

E. G.

Action of Methyl Alcoholic Potash on 2-Nitronaphthalene.

JAKOB MEISENHEIMER and KLAUS WITTE (*Ber.*, 1903, 36, 4164—4174. Compare Abstr., 1902, i, 795).—2-Nitronaphthalene is not affected by cold methyl alcoholic potash, but with the concentrated alkali for 4 or 5 hours at 55° a considerable amount goes into solution, and when the clear liquid is acidified, β-naphthaquinone-2-oxime is obtained. It melts at 162—164°, and not at 147—148° (Worms, Abstr., 1883, 69), or at 152° (Goldschmidt, *ibid.*, 1884, 1137).

The benzoyl derivative melts at 189—190°, and not at 162°. The p-*nitrobenzyl* derivative crystallises in long, yellow needles melting at 199°.

β-Naphthaquinone-2-oxime-dimethylacetal, $C_{10}H_6(OMe)_2{:}N{\cdot}OH$, is obtained when the alkaline solution is diluted with ice and water and treated with carbon dioxide in place of a mineral acid. It crystallises in large, colourless plates melting at 126°, is readily soluble in most organic solvents, and on treatment with mineral acids, or even with alkalis, yields the oxime melting at 162—164°. Its *methyl ether*

is a liquid, its p-*nitrobenzyl* derivative melts at 97—98°, and its *benzoate* at 189—190°.

Other products obtained by the action of methyl alcoholic potash on 2-nitronaphthalene are 1 : 1-dinaphtha-2 : 2-*o*-diazine oxide, 2 : 2-azoxynaphthalene, and a product crystallising in red needles, very sparingly soluble in acetic acid, and melting and decomposing at 243°. On reduction, it yields *as*-1 : 2-naphthazine, and appears to be a mixture of this with oxy-derivatives. J. J. S.

Preparation of Isomeric Sulphonic Acids by means of Catalytic Agents. M. Iljinsky (*Ber.*, 1903, 36, 4194—4200).—When mercury or its salts are employed as catalytic agents in the sulphonation of anthraquinone, not only does sulphonation take place very much more easily, but other products are formed. Thus, besides the new *anthraquinone-α-monosulphonic acid*, which forms characteristic calcium and potassium salts and is converted on heating with milk of lime into erythroxyanthraquinone, a mixture of 1:5-, 1:8-, 1:7-, and perhaps 1 : 6-disulphonic acids is formed. The conditions for obtaining the 1:7-disulphonic acid in quantity are described, and the method greatly facilitates the technical production of 1:7-dihydroxyanthraquinones. E. F. A.

Preparation of Hydroxyanthraquinones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 145238).—Nitroanthraquinones are readily converted into the corresponding hydroxy-compounds by heating with pyridine. The preparation of anthrarufin from 1 : 5-dinitroanthraquinone, and of chrysazin from 1 : 8-dinitroanthraquinone, is described. Picoline, lutidine, or collidine, or unfractionated mixtures of these bases, may be employed in place of pyridine. C. H. D.

Essence of Geranium from Cannes. Paul Jeancard and C. Satie (*Bull. Soc. chim.*, 1904, [iii], 31, 43—49).—The influence of atmospheric conditions on the composition of the essence obtained from the leaves of *Pelargonium odoratissimum* has been studied. The effect of cold nights is to diminish the proportion of alcohols in the essence, but this diminution is not accompanied by a more active esterification; it is therefore due to a decrease in the amount of essence contained in the leaf. The amount of geraniol and citronellol varies; the former decreases, whilst the latter increases in cold weather. The physical constants, rotatory power, specific gravity, solubility, and viscosity do not vary much. S. S.

Constitution of Tanacetone [Thugone], $C_{10}H_{16}O$. Friedrich W. Semmler (*Ber.*, 1903, 36, 4367—4372. Compare Abstr., 1900, i, 240, 452, 676).—*Benzylidenetanacetone*, $CH_2<\begin{matrix}CH\text{——}CHMe \\ |\qquad\qquad \\ CPr^{\beta}\cdot C(CHPh)\end{matrix}>CO$, prepared by condensing tanacetone with benzaldehyde in presence of sodium ethoxide, boils at 178° under 9 mm. pressure; on oxidation, it is quantitatively decomposed into *benzoic acid* and *homotanacetonedicarb-*

oxylic acid, $CH_2<\begin{matrix}CH\cdot CHMe\cdot CO_2H\\ |\\ CPr^{\beta}\cdot CO_2H\end{matrix}$, which melts at 148° and forms an *anhydride*, $C_{10}H_{14}O_3$, boiling at 157—158° under 15 mm. pressure. *Dihydrobenzylidenetanacetyl alcohol*,

$$CH_2<\begin{matrix}CH \text{———} CHMe\\ |\\ CPr^{\beta}\cdot CH(CH_2Ph)\end{matrix}>CH\cdot OH,$$

formed from the ketone by reduction with sodium and alcohol, is fully saturated; it boils at 181—182° under 15 mm. pressure. *Dihydrobenzylidenetanacetone*, $C_{17}H_{22}O$, formed from this by oxidising with chromic acid, boils at the same temperature; the *semicarbazone* melts at 195°, and the *amine* boils at 185—190° under 25 mm. pressure. *Benzylidenetanacetonehydroxylamine*, $C_{17}H_{20}O_2,NH_2\cdot OH$, boils at 138—140°. E. F. A.

Fate of Cyclic Terpenes and Camphor in the Animal System. IV. Behaviour of Sabinol. EMIL FROMM and PAUL CLEMENS (*Zeit. physiol. Chem.*, 1903, **45**, 251—262. Compare Abstr., 1902, ii, 159, 341; 1903, i, 429).—The compound previously described as sabinolglycuronic acid is best obtained by treating the urine, after ingestion of sabinol, with basic lead acetate, when a mixture of a basic lead salt with basic lead chloride is obtained; this is then decomposed with barium sulphide solution, and ultimately carefully neutralised with dilute sulphuric acid. The barium salt has not the composition of barium sabinolglycuronate, and the acid obtained by hydrolysis with sulphuric acid does not give Neuberg's test for glycuronic acid (Abstr., 1901, i, 66); it is probably a *penturonic acid*, $C_5H_8O_6$. Its *anhydride* begins to turn brown at 145°, and melts at about 168°, is fairly readily soluble in alcohol, and yields a *semicarbazide* melting and decomposing at 205°. J. J. S.

Sugar Components of Solanin and Convallamarin. EMIL VOTOČEK and R. VONDRÁČEK (*Ber.*, 1903, **36**, 4372—4373. Compare Abstr., 1903, i, 570; also Zeisel and Wittmann, this vol., i, 80).—Solanin and convallamarin contain dextrose, rhamnose, and a hexose of which the phenylmethylhydrazone melts at 187—188°. This is shown to be identical with galactose, the phenylmethylhydrazone of which Lobry de Bruyn and van Ekenstein found to melt at 180°; it is now shown, however, that it melts at 188°.

E. F. A.

Action of Hydrochloric Acid on Artemisin. PASQUALE BERTOLO (*Atti R. Accad. Lincei*, 1903, [v], **12**, ii, 273—278. Compare Abstr., 1901, i, 718, and 1902, i, 814).—The action of concentrated hydrochloric acid on artemisin gives rise to a compound, $C_{15}H_{16}O_3$, termed by the author *artemisic acid*, which is very soluble in alcohol, ether, light petroleum, or dilute acetic acid, and crystallises from the last-named in shining needles melting at 135—136°; it has the normal molecular weight in freezing acetic acid, and has $[\alpha]_D + 70{\cdot}4°$ in alcoholic solution; the *barium* (soluble in water), *silver*, *lead*, *copper*, and *mercuric* salts were prepared; the *methyl* ester was obtained as a

dense oil very readily soluble in the ordinary organic solvents. The *ethyl* ester separates from light petroleum in hard, transparent prisms, which melt at 97—98°, and dissolve in alcohol, ether, or ethyl acetate; it is insoluble in alkali carbonate solutions, but dissolves in cold potassium hydroxide solution, from which carbon dioxide reprecipitates it; it gives no oxime or phenylhydrazone, but forms a benzoyl derivative. This behaviour indicates that the ethyl ester contains a phenolic hydroxyl group, the presence of which is confirmed by the action on artemisic acid of fused potassium hydroxide, which yields *p*-dimethylnaphthol. The latter is only obtained from those derivatives of santonin or artemisin which contain such a hydroxyl group (Abstr., 1903, i, 261). T. H. P.

Substances accompanying the Oil in Sesamé Seeds. Francesco Canzoneri and F. Perciabosco (*Gazzetta*, 1903, **33**, ii, 253—260. Compare Villavecchia and Fabris, Abstr., 1898, i, 445).—By a process of fractional extraction and crystallisation using various solvents, the authors have isolated, in addition to sesamin and the alcohol resembling cholesterol, a *substance* X, which crystallises from light petroleum in nacreous laminæ, melts at 91—92°, and is not changed when boiled with concentrated alkalis; its composition may be expressed by any of the formulæ $C_{23}H_{24}O_7$, $C_{22}H_{22}O_7$, $C_{13}H_{14}O_4$. It is readily attacked by cold concentrated hydrochloric acid, forming a red oil which gives in a marked degree the colour reaction with furfuraldehyde characteristic of oil of sesamé, and reduces immediately ammoniacal silver nitrate; when exposed to the air, it is oxidised to a *substance* which crystallises from alcohol in lustrous plates and melts at 185—186°.

The substance which Villavecchia and Fabris considered to have the composition $C_{25}H_{44}O,H_2O$, contrary to their statements does not lose its water in a vacuum over sulphuric acid, but only after six hours' heating at 110°; dried at this temperature, it has the composition, $C_{26}H_{44}O,\frac{1}{2}H_2O$, of an *iso*cholesterol. W. A. D.

Does Capaloin contain Methoxyl? [Alexander Tschirch and] K. G. v. Küylenstjerna (*Arch. Pharm.*, 1903, **241**, 689—690. Compare Abstr., 1901, i, 602).—Portions of a crude specimen of capaloin were recrystallised respectively from methyl alcohol, ethyl alcohol, and acetone, and were examined by Zeisel's method; they contained 9·76, 9·38, and 9·44 per cent. of methoxyl respectively. The formula $C_{15}H_{13}O_6 \cdot OMe$ requires 9·68 per cent. Léger's inability to detect methoxyl in the substance is thus left unexplained.

C. F. B.

Brazilin from Brazilein. Josef Herzig and Jacques Pollak (*Ber.*, 1903, **36**, 3951—3953).—In preparing the triacetyl derivative, $C_{16}H_9O(OAc)_3$, already known, by reductive acetylation (Abstr., 1902, i, 482), acetylbrazilin was obtained to the extent of about 12 per cent. of the brazilein employed. This fact, which indicates a direct conversion of brazilein into brazilin, removes the principal objection to the quinoidal formula for brazilein. W. A. D.

Pigments of Geranium and other Plants. Arthur B. Griffiths (*Ber.*, 1903, 36, 3959—3961).—The pigments of the petals of geranium, helianthus, and verbena were isolated by extracting with alcohol and evaporating the solution to dryness in a vacuum. The absorption spectra of the pigments are described.

The pigments of helianthus and verbena contain carbon, hydrogen, oxygen, nitrogen, and sulphur; to that of geranium, which is crystalline, the composition $C_{15}H_{10}O_6$ is assigned, and it yields a crystalline *potassium* salt, $C_{15}H_8O_6K_2$, and a *diacetyl* derivative crystallising from methyl alcohol in red needles and melting at 125°. This pigment in alcoholic solution has $[\alpha]_D$ $-74·97°$, whilst the specific rotations of the pigments of verbena and helianthus are respectively $-85·39°$ and $-59·28°$. All three pigments in alcoholic solution apparently emit radiations which diminish the electrical resistance of selenium. W. A. D.

Nile-blue-base as a Reagent for Atmospheric Carbon Dioxide. The Action of Acid Dyes on Cellulose, Alcohol, and Acetone, and Theory of Dyeing Histological Preparations. Martin Heidenhain (*Pflüger's Archiv*, 1903, 100, 217—241. Compare Abstr., 1902, i, 651, and L. Michaelis, *Pflüger's Archiv*, 1903, 97, 634).—The author adheres to his view that the colorations of proteids are largely due to chemical causes and not mainly to physical (solid solutions), as suggested by Witt and by Michaelis. The main objections are: (1) that most of the best dyes employed are colloidal and as such would not pass (dialyse) readily into the proteid. (2) That animal tissues, although much more active than textile fabrics, are not such good solvents as compared with water. (3) That basic aniline dyes are much more readily removed by tissues from alcoholic than from aqueous solutions, although they are less soluble in water than in alcohol.

Michaelis' statement that eosin yields pale yellow solutions with benzene, toluene, xylene, and chloroform which turn a brilliant red when poured on to filter-paper is correct, but the change in colour is due to the acid action of atmospheric carbon dioxide.

Methyl and ethyl alcohols and acetone dissolve the acid to form pale yellow solutions provided no trace of carbon dioxide is present. Nile-blue-base behaves in a very similar manner, yielding reddish-brown solutions which turn blue in presence of small amounts of carbon dioxide. This reagent is a remarkably good one for carbon dioxide. The author confirms Michaelis' results on the behaviour of alcohol, acetone, and cellulose towards acid dyes. They produce with the free sulphonic acids of benzopurpurin and congo-red changes in colour similar to those produced by alkalis and by proteids. The readiness with which the change occurs depends to a large extent on the relative strength of the acid dye, and is regarded in all cases as being of a chemical nature. A kind of ester formation is suggested. Phenol, cresol, creosote, and aniline water all behave in a similar manner towards these acid dyes. The anhydrous reagents are not able to bring about the same colour changes. J. J. S.

New Syntheses effected by the Aid of Compounds containing the Methylene Group attached to One or Two Acid Radicles. Action of Epichlorohydrin on the Sodium Derivative of Acetylacetone. III. ALBIN HALLER and GEORGES BLANC (*Compt. rend.*, 1903, 137, 1203—1205. Compare Abstr., 1901, i, 538; 1903, i, 318).—By the prolonged action of epichlorohydrin on the sodium derivative of acetylacetone at the temperature of the water-bath, condensation occurs with the formation of sodium chloride, ethyl acetate, and a new alcohol, $C_6H_{10}O_2$, for which the authors suggest the constitution

$$\begin{matrix} CH\cdot CH_2 \\ \| \\ CMe—O \end{matrix} > CH\cdot CH_2\cdot OH \text{ or } CMe < \begin{matrix} CH\cdot CH_2 \\ O—CH_2 \end{matrix} > CH\cdot OH.$$

It is a colourless, mobile liquid which boils at 70° under 8 mm. pressure or at 81—82° under 15 mm. pressure, has a sp. gr. 0·988 at 14°/4° and n_D 1·447 at 14°; it is very soluble in all solvents except light petroleum, and has an agreeable odour; the molecular refraction agrees with that calculated for a compound of the above constitution. The alcohol is easily resinified by alkalis and acids, and does not yield crystalline derivatives with ammonia or phenylcarbimide. The acetyl derivative, C_6H_9OAc, is a colourless liquid boiling at 190—195° and is insoluble in water; a hydrogenated methyl ether, $C_7H_{14}O_2$, has been prepared by the action of methyl iodide and sodium on an ethereal solution of the alcohol; it is an oil insoluble in water and boiling at 160—170° and having an odour resembling that of cineol.

By spontaneous change during several months, or more rapidly in the presence of traces of alkali, the alcohol is transformed into an isomeric ketone boiling at 70—75° under 15 mm. pressure; it has a strong odour and is insoluble in water; it forms two semicarbazides according as the condensation is effected in dilute or concentrated solutions; the former crystallises in beautiful, white needles melting at 116° and is soluble in water; the latter crystallises in small, colourless prisms melting and decomposing at 280°, and is almost insoluble in all ordinary solvents. M. A. W.

a-*m*-Tolyloxy-β-furylacrylic Acid. RAFFAELE PALADINO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1903, [iii], 9, 195—201).—a-m-*Tolyloxy-β-furylacrylic acid*, $C_4OH_3\cdot CH:C(O\cdot C_6H_4Me)\cdot CO_2H$, prepared by heating furfuraldehyde (1 mol.) with sodium *m*-tolylglycollate (1 mol.) and about four times its weight of acetic anhydride, separates from 50 per cent. alcohol in masses of yellowish-white needles melting at 160—161°; it is readily soluble in light petroleum, ether, or alcohol, but only slightly so in water. Its *anhydride*,

$$O[CO\cdot C(O\cdot C_6H_4Me):CH\cdot C_4OH_3]_2,$$

obtained by the action of phosphoric oxide on a light petroleum solution of the acid, is deposited from alcohol in minute, pale yellow crystals which are soluble in ether and melt at 149°. The *aniline* salt, $C_{14}H_{12}O_4.PhNH_2$, separates from alcohol in yellow crystals melting at 151° and soluble in light petroleum or chloroform. The *phenyl* ester, $C_{14}H_{11}O_4Ph$, is deposited from chloroform or ether in microscopic crystals melting at 151°. T. H. P.

Phenylated Coumarones. RICHARD STOERMER [with M. REUTER] (*Ber.*, 1903, 36, 3979—3986).—1-*Phenylcoumarone*, $C_6H_4<\overset{-O-}{CH}\gg CPh$, prepared from salicylaldehyde, phenylchloroacetic acid, and sodium hydroxide, crystallises from dilute alcohol in silvery flakes with a faint odour of hyacinths, and melts at 120—121°. 4-*Bromo*-1-*phenylcoumarone*, $C_6H_3Br<\overset{-O-}{CH}\gg CPh$, prepared in a similar manner from bromosalicylaldehyde, melts at 148°. 1-*Phenylcoumaran*, $C_6H_4<\overset{-O-}{CH_2}>CHPh$, prepared by reducing 1-phenylcoumarone with sodium and alcohol or by condensing salicylaldehyde benzyl ether with sodium, solidifies to white crystals which melt at 32°; *o-hydroxydibenzyl*, $HO\cdot C_6H_4\cdot CH_2\cdot CH_2Ph$, formed as a by-product in the reduction, crystallises from alcohol in white flakes and melts at 83·5°.

1-*Chloro-2-phenylcoumarone*, $C_6H_4<\overset{-O-}{CPh}\gg CCl$, prepared by the action of phosphorus oxychloride on the lactone of *o*-hydroxydiphenylacetic acid, $C_6H_4<\overset{-O-}{CHPh}>CO$, boils at 179° (corr.) under 13 mm. and at 191° under 18 mm. pressure; the chlorine cannot be removed by sodium amalgam, by zinc and acetic acid, or by zinc and alcoholic hydrochloric acid. Sodium and alcohol reduce the chloro-compound to 2-*phenylcoumaran*, $C_6H_4<\overset{-O-}{CHPh}>CH_2$, which crystallises from hot alcohol in stout, white needles, melts at 38·5°, and boils at 167° (corr.) under 14 mm. pressure. When the preceding compound is reduced with hydrogen iodide, it gives a small yield of a *phenol*, $C_{14}H_{14}O$, which crystallises from alcohol and melts at 63°; the *phenylurethane*, $C_{21}H_{19}O_2N$, crystallises from benzene and alcohol and melts at 139°; the nature of the phenol is discussed later (Stoermer and Kippe, following page). T. M. L.

Phosphorus Tribromide as a Reducing Agent. RICHARD STOERMER (*Ber.*, 1903, 36, 3986—3992).—Phosphorus tribromide reduces hydroxydiphenylacetic lactone, $C_6H_4<\overset{-O-}{CHPh}>CO$, to 2-phenylcoumarone, $C_6H_4<\overset{-O-}{CPh}\gg CH$, deoxybenzoin to stilbene, 1-phenyl-3-methylpyrazolone, $NPh<\begin{matrix}N{=}CMe\\ CO\cdot CH_2\end{matrix}$, to phenylmethylpyrazole,

$$NPh<\begin{matrix}N{=}CMe\\ CH{:}CH\end{matrix},$$

1 : 3-diphenylpyrazolone to 1 : 3-diphenylpyrazole (yield 85 per cent.), and carbostyril in part to quinoline. In the case of 1-phenyl-3 : 4 : 4-trimethylpyrazolone, $NPh<\begin{matrix}N{=}CMe\\ CO\cdot CMe_2\end{matrix}$, phosphorus tribromide causes the migration of a methyl group, and 1-phenyl-3 : 4 : 5-trimethyl-

pyrazole, $NPh<\begin{smallmatrix}N=\!=\!=CMe \\ CMe:CMe\end{smallmatrix}$, is produced; so also the 2-phenylcoumarone produced from the lactone referred to above is accompanied by 1-phenylcoumarone, indicating that the tribromide brings about a displacement of the phenyl group. T. M. L.

Syntheses, Isomeric Changes, and Decompositions of Phenylated Coumarones and Coumarans. RICHARD STOERMER and OTTO KIPPE (*Ber.*, 1903, 36, 3992—4013).—When heated with alcoholic potassium hydroxide at 200°, 2-phenylcoumaran,

$$C_6H_4<\begin{smallmatrix}-O- \\ CHPh\end{smallmatrix}>CH_2,$$

yields ethylene, hydrogen, and a little *o*-hydroxydiphenylacetic acid (oxidation product), but is for the most part converted into the isomeric *o-hydroxy-αα-diphenylethylene*, $CH_2:CPh\cdot C_6H_4\cdot OH$, a colourless oil, which boils at 167° under 13 mm., at 169—170° under 14 mm., or at 180° under 22 mm. pressure, has a sp. gr. 1·1129 at 18° and n_D 1·6193 at 18°. The *sodium* derivative separates on adding 30—40 per cent. sodium hydroxide to the phenol, and can be extracted by means of ether; the sodium derivative of carvacrol behaves in a similar manner. The *phenylurethane*, $C_{21}H_{17}O_2N$, crystallises from light petroleum in thin, felted needles and melts at 105°; when crystallised from dilute alcohol, the composition of the substance is unaltered, but the melting point falls to 86°, and cannot be again raised by crystallising from light petroleum. The *methyl* ether, *α-o-anisyl-α-phenylethylene* [*o*-methoxy-αα-diphenylethylene], $CH_2:CPh\cdot C_6H_4\cdot OMe$, separates from alcohol in white needles, melts at 35°, and boils at 166° under 14 mm. pressure. It was also prepared synthetically by the action of magnesium on iodoanisole, $C_6H_4I\cdot OMe$, and acetophenone, and hydrolysis of the product by alcoholic potassium hydroxide at 200°.

1-*Chloro-2-phenyl-4-methylcoumarone*, $C_6H_3Me<\begin{smallmatrix}-O- \\ CPh\end{smallmatrix}\gg CCl$, prepared by the action of phosphorus oxychloride on the lactone of phenyl-*p*-hydroxytolylacetic acid, crystallises in long needles, melts at 66·5°, and boils at 194° under 16 mm. pressure. It is reduced by sodium and alcohol to *2-phenyl-4-methylcoumaran*,

$$C_6H_3Me<\begin{smallmatrix}-O- \\ CHPh\end{smallmatrix}>CH_2,$$

which crystallises from alcohol in glistening, prismatic needles, melts at 57°, and boils at 184° under 18 mm. pressure. Like the lower homologue, it undergoes isomeric change when heated with alcoholic potash and is converted into *α-phenyl-α-p-hydroxytolylethylene*,

$$CH_2:CPh\cdot C_6H_3Me\cdot OH\ [Me:OH:C=1:4:3],$$

which boils at 172—174° under 10 mm. or at 187° under 20 mm. pressure, has a sp. gr. 1·0852 at 20°, n_D 1·6075 at 20°; the *sodium* derivative, like that just described, can be extracted by ether from the alkaline solution; the *phenylurethane*, $C_{22}H_{19}O_2N$, crystallises from light petroleum and from dilute alcohol in glistening needles, which in each case melt constantly at 101°.

2-Phenylcoumarone could not be prepared by internal condensation of phenoxyacetophenone, $OPh\cdot CH_2\cdot COPh$, or by reducing its

1-chloro-derivative, or by the action of magnesium on *o*-bromophenoxyacetophenone, $C_6H_4Br{\cdot}O{\cdot}CH_2{\cdot}COPh$, but was finally synthesised from the hydroxydiphenylethylene prepared from 2-phenylcoumaran. o-*Acetoxy-aa-diphenylethylene*, $OAc{\cdot}C_6H_4{\cdot}CPh{:}CH_2$, boils at 172—173° under 8 mm. or at 177° under 10 mm. pressure. The *dibromide*, $OAc{\cdot}C_6H_4{\cdot}CPhBr{\cdot}CH_2Br$, crystallises from light petroleum in glistening prisms and melts at 83°. 2-*Ethoxy-2-phenylcoumaran*, $C_6H_4{<}\overset{\text{——O——}}{\text{CPh(OEt)}}{>}CH_2$, prepared by the action of sodium ethoxide on the dibromide, crystallises from hot alcohol in white, glistening flakes and melts at 88—89°. 2-*Phenylcoumarone*, $C_6H_4{<}\overset{\text{—O—}}{\text{CPh}}{\geqslant}CH$, prepared by heating the preceding compound, boils at 177—178° under 15 mm. or at 316—317° (corr.) under 760 mm. pressure, has a sp. gr. 1·1449 at 19°, n_D 1·6313 at 20°, and solidifies to a crystalline mass which melts at 12—13°; a modification melting at 42° is sometimes produced and the "dimorphism" is compared with that of benzophenone or hydroxyphenylacetic lactone. 2-Phenylcoumarone is also produced when hydroxydiphenylacetic lactone is heated with phosphorus tribromide at 200° in an oil-bath, whilst heating in a sealed tube yields 1-phenylcoumarone; 2-phenylcoumarone is also produced by heating the lactone with phosphorus pentasulphide at 210°.

o-*Anisylphenylethane* [o-*methoxy-aa-diphenylethane*], $OMe{\cdot}C_6H_4{\cdot}CPhMe$, prepared by reducing *o*-methoxydiphenylethylene with sodium and alcohol, is a colourless liquid of camphor-like odour, boils at 160—161° under 11 mm. pressure, and solidifies to crystals melting at 26°. o-*Hydroxy-aa-diphenylethane*, $OH{\cdot}C_6H_4{\cdot}CPhMe$, prepared by hydrolysing the ether with alcoholic potassium hydroxide at 200°, boils at 177—178° under 12 mm. pressure, has a sp. gr. 1·0778 at 20°, and n_D 1·5868; the *sodium* derivative separates from the strongly alkaline solution, and can be extracted with ether; the *phenylurethane* crystallises from dilute alcohol or from light petroleum in white, glistening needles and melts at 99°.

p-*Hydroxydibenzyl*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2Ph$, prepared by hydrolysing its methyl ether with alcoholic potash at 200°, crystallises from dilute alcohol in glistening flakes and melts at 100—101°; the *phenylurethane* crystallises from alcohol or light petroleum in glistening, white flakes and melts at 150°. The phenol obtained by Stoermer and Reuter (this vol., i, 181), by the action of hydrogen iodide on 2-phenylcoumaran, is isomeric with the two preceding phenols, but is not identical with either, and its nature is at present unknown; a hydrocarbon which was also produced in the same interaction has been identified as β-phenylnaphthalene; this hydrocarbon, which is also produced by the action of hydrogen iodide on phenoxystyrene, $CHPh{:}CH{\cdot}OPh$, is probably formed by hydrolysis of the 2-phenylcoumaran, by addition of 2HI, to phenol and styrene di-iodide, $C_6H_5{\cdot}CHI{\cdot}CH_2I$, and condensation of two mols. of the di-iodide with elimination of 4HI to form phenylnaphthalene.

It was thought that *o*-hydroxydiphenylethylene might be reduced with hydrogen iodide to the *o*-hydroxydiphenylethane just described, just as styrene is reduced to ethylbenzene, but the actual product is the

para-compound (Koenigs and Carl, Abstr., 1892, 446), which is probably formed by reduction to styrene and phenol, as these condense to form the parahydroxy-compound, although the ortho-compound is also found in the condensation product; the *phenylurethane*, $C_{21}H_{19}O_2N$, of *p*-hydroxydiphenylethane crystallises from light petroleum in glistening, white needles and melts at 111°. T. M. L.

Syntheses of 3 : 4-Dihydroxyflavone. GERTRUD WOKER, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1903, 36, 4235—4244).—The compounds prepared by Friedländer and Rüdt by condensing *a*-chloro-*o*-hydroxyacetophenone with aromatic aldehydes, and formulated by them as flavones derived from the compound

$$C_6H_4<\begin{matrix}O-CPh\\ \quad\;\, \| \\ CO\cdot CH\end{matrix}$$

(Abstr., 1896, i, 439), have been shown by Kostanecki and his pupils to be oxindogenide derivatives $C_6H_4<\begin{matrix}O\\CO\end{matrix}>C:CHPh$ (Abstr., 1896, i, 606); final proof of this view is afforded by the synthesis of 3 : 4-dihydroxyflavone, which has been found to be isomeric, and not identical with Friedländer's compound.

2′-*Hydroxy*-3′ : 4′-*dimethoxychalkone*, $OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH:CHPh$, prepared from gallacetophenone dimethyl ether and benzaldehyde, crystallises from dilute alcohol in long, golden-yellow needles, and melts at 98°. The *acetyl* derivative, $C_{19}H_{18}O_5$, crystallises from alcohol in long needles and melts at 110°; its *dibromide*, $C_{19}H_{18}O_5Br_2$, crystallises from alcohol in white prisms and melts at 140°. 3′ : 4′-*Dimethoxyflavone*, $C_6H_2(OMe)_2<\begin{matrix}O-CPh\\ \quad\;\, \| \\ CO\cdot CH\end{matrix}$, prepared by the action of alcoholic potassium hydroxide on the preceding compound, crystallises from alcohol in white needles, melts at 151°, and yields benzoic acid and gallacetophenone dimethyl ether, when boiled with sodium ethoxide. 3 : 4-*Dihydroxyflavone*, $C_6H_2(OH)_2<\begin{matrix}O-CPh\\ \quad\;\, \| \\ CO\cdot CH\end{matrix}$, crystallises from 50 per cent. alcohol in very pale yellow needles and melts at 239°. The *acetyl* derivative, $C_{19}H_{14}O_6$, crystallises from alcohol in white needles and melts at 193°.

3 : 4-*Dimethoxyflavanone*, $C_6H_2(OMe)_2<\begin{matrix}O-CHPh\\ \quad\;\, | \\ CO\cdot CH_2\end{matrix}$, prepared by the direct action of sodium hydroxide on an alcoholic solution of benzaldehyde and gallacetophenone dimethyl ether, crystallises from methyl alcohol in white needles and melts at 115°. The *bromo*-derivative, $C_{17}H_{15}BrO_4$, crystallises from alcohol in needles and melts at 110°; when acted on by alcoholic potassium hydroxide, it also yields dihydroxyflavone, thus affording a second method of synthesis.

T. M. L.

Bromine Derivatives of the Cinchona Alkaloids and the corresponding Compounds containing less Hydrogen. A. CHRISTENSEN (*J. pr. Chem.*, 1903, [ii], 68, 425—448. Compare Abstr., 1901, i, 481).—The dibromides of quinine, cinchonine, and cinchonidine are best prepared by adding bromine to the alkaloid in hydrogen

bromide and glacial acetic acid solution. From the hydrobromides so obtained, the dibromides are liberated on addition of aqueous sodium hydroxide. When acted on by alcoholic potassium hydroxide, these dibromides easily lose HBr, being converted into the monobromo-substitution derivatives of the alkaloids, which again lose HBr on prolonged boiling with alcoholic potassium hydroxide, and yield the dehydro-alkaloids (Koenigs and Comstock, Abstr., 1892, 1010).

With bromine in aqueous solution, cinchonine dibromide hydrobromide forms the perbromide, which dissolves on boiling to a red solution with green fluorescence. On addition of more bromine and cooling, a *substance* is obtained as an orange-coloured precipitate. In alcoholic solution, the substance is red by transmitted, green by reflected light, the aqueous solution has a yellowish-green fluorescence, and gives a red to violet precipitate with ammonia. Similar results are obtained with cinchonidine dibromide.

Bromocinchonine, $C_{19}H_{21}ON_2Br$, crystallises in long needles or long, thin, rhombic plates, melts and becomes brown at 225—226°, and has $[\alpha]_D$ +185·7° at 17°. On treatment with zinc and dilute sulphuric acid, bromocinchonine gradually loses bromine. The *hydrochloride*, $C_{19}H_{21}ON_2Br,HCl,2H_2O$, crystallises in long, thin leaflets; the *hydrobromide*, $C_{19}H_{21}ON_2Br,2HBr$, crystallises in rhombic plates and blackens and melts at 258°; the *oxalate*, $(C_{19}H_{21}ON_2Br)_2,C_2H_2O_4,7H_2O$, crystallises in quadratic needles, becomes anhydrous at 110°, and is only slightly soluble in water, but easily so in alcohol. The author has compared Koenig's and Comstock's dehydrocinchonine hydrobromide (Abstr., 1887, 1123), and found it to be identical with bromocinchonine. A repetition of Laurent's work (*Compt. rend.*, 1849, **29**, 312) shows his dibromocinchonine to be identical with cinchonine dibromide, and his sesquibromocinchonine to be a mixture of the dibromide with bromocinchonine.

Kopp's oxycinchonine, sesquioxycinchonine, and dioxycinchonine (*Arch. Pharm.*, 1876, **209**, 34), obtained from Laurent's supposed three bromo-compounds, were most probably impure dehydrocinchonine.

G. Y.

Corydalis Alkaloids. JOHANNES GADAMER (*Arch. Pharm.*, 1903, **241**, 630—634).—An introduction to the following paper.

C. F. B.

Corybulbine and *iso*Corybulbine. DANIEL BRUNS (*Arch. Pharm.*, 1903, **241**, 634—655. Compare Abstr., 1901, i, 288; 1902, i, 306).—From 20 kilos. of *Corydalis cava* tubers, 5·75 per cent. of alkaloids was obtained, exclusive of corytuberine; only 0·185 per cent. of corybulbine was obtained in the impure state. It was purified by floating alcohol on a saturated (about 1 per cent.) solution of the alkaloid in chloroform; the melting point 237—238° and composition $C_{21}H_{25}O_4N$ were confirmed; it has $[\alpha]_D$ + 303°, and is very sensitive to light. It is a monoacid base: the crystalline *hydrochloride* melts and decomposes at 245—250°; the *aurichloride* and *platinichloride* are amorphous, and could only be obtained of normal composition by adding a saturated

solution of the hydrochloride to excess of aqueous gold or platinum chloride.

Dehydrocorybulbine, $C_{21}H_{21}O_4N$, a monoacid base, melting at 210—211°, was obtained from the corybulbine by the action of iodine in alcoholic solution; the crystalline *hydrochloride* and *platinichloride* melt at 225—227° and 236° respectively. If the iodide is mixed with 10 per cent. aqueous sodium hydroxide, the mixture warmed until the crystals which separate have redissolved, and the crystals which separate again on cooling recrystallised from water, *dehydrocorybulbine*, $C_{18}H_{12}(OMe)_3ON,5H_2O$, is obtained in dark reddish-violet needles which melt at 175—178°. Only $4H_2O$ are removed by drying over sulphuric acid; the 5th mol. is only removed by prolonged drying at 95° in a vacuum (heating in air brings about decomposition). Unlike berberine (Schmidt, Abstr., 1884, 339) and dehydrocorydaline (Ziegenbein, Abstr., 1897, i, 175), the substance has not the character of a ψ-ammonium base: it is not soluble in ether; it does not form compounds with chloroform, acetone, or ammonium sulphide, and it has no alkaline reaction. Evidently it is a phenolbetaine, water having been eliminated between the phenolic hydroxyl and that attached to the nitrogen atom.

If this view is correct, an acid derivative of dehydrocorybulbine, which would no longer contain the phenolic hydroxyl, should exhibit a different behaviour. An acetyl derivative could not be obtained, but *benzoyldehydrocorybulbine* was prepared by the Schotten-Baumann reaction. This melts at 173—174°, whilst its yellow *hydrochloride*, $C_{21}H_{20}BzO_4N,HCl,2H_2O$, remains unmelted at 250°, and its yellow *nitrate* melts at 230—231°; it does form crystalline *additive compounds* with 1 mol. each of chloroform and acetone, melting at 176° and 201—202° respectively, and with yellow ammonium sulphide. Attempts to prepare an oxime from it were unsuccessful.

i-Corybulbine, obtained by the reduction of dehydrocorybulbine (Abstr., 1901, i, 288), forms a *hydrochloride*, also a *nitrate* melting at 207—208°; the *platinichloride* and the *aurichloride*, the latter melting at 223°, were obtained by filtering a solution of the hydrochloride into excess of aqueous platinum or gold chloride. An attempt to resolve the base into optically active isomerides by crystallisation of its bromocamphorsulphonate was unsuccessful.

*iso*Corybulbine, $C_{21}H_{25}O_4N$ (Gadamer and Ziegenbein, Abstr., 1902, i, 307), has $[\alpha]_D + 299{\cdot}8°$; when heated for a day with iodine at 95—100° in alcoholic solution, it is oxidised to *dehydro*iso*corybulbine*. The *hydriodide* of this base, $C_{21}H_{21}O_4N,HI$, and the *nitrate* do not melt at 260°. The hydriodide yields a crystalline precipitate, presumably of the free base, when it is treated with aqueous sodium hydroxide; zinc and sulphuric acid reduce it to inactive i-iso*corybulbine*, which melts at 165—167°.

apo-Corydaline was prepared by boiling corydaline with hydriodic acid of sp. gr. 1·7 (Dobbie and Lauder, Trans., 1892, 609), and converted into the *hydrochloride*, $C_{18}H_{19}O_4N,HCl$, which melts and decomposes at 220—222°; neither an aurichloride nor a platinichloride could be prepared, owing to the reducing action of the base. The same hydrochloride was obtained in a similar manner from corybulbine and *iso*corybulbine. Hence these substances must be regarded as isomerides

with the formula $C_{18}H_{15}N(OMe)_3 \cdot OH$, differing only in the positions of the OMe and OH groups, whilst corydaline must be regarded as $C_{18}H_{15}N(OMe)_4$, the group $C_{18}H_{15}N$ being the same in all three substances.

It is possible that *iso*corybulbine is not contained in the tubers, but is formed from corydaline during the working up of the tubers, when the solution of the uncrystallisable bases in light petroleum is treated with gaseous hydrogen chloride. C. F. B.

Cotarnine. IV. Application of Grignard's Reaction. MARTIN FREUND (*Ber.*, 1903, 36, 4257—4259. Compare Abstr., 1902, i, 556; 1903, i, 572).—*a-Methylhydrocotarnine*, prepared by the action of magnesium methiodide, was obtained as a viscous liquid. The *hydriodide*, $C_{13}H_{17}NO_3,HI$, crystallises from hot water in needles and melts at 178—180°. The *hydrobromide*, $C_{13}H_{17}NO_3,HBr$, crystallises in needles and melts at 199—200°. The *hydrogen sulphate*,

$$C_{13}H_{17}NO_3,H_2SO_4,$$

crystallises in needles and melts at 155°. The *platinichloride*,

$$(C_{13}H_{17}NO_3)_2,H_2PtCl_6,$$

crystallises from alcohol and melts at 220°. The *methiodide*,

$$C_{13}H_{17}NO_3MeI,$$

separates from hot water in long, glistening crystals and melts at 228—229°. T. M. L.

Sparteine Sulphate. CHARLES MOUREU and AMAND VALEUR (*J. Pharm. Chim.*, 1903, [vi], 18, 545—546).—The salt has the formula $C_{15}H_{26}N_2,H_2SO_4,5H_2O$. In aqueous solution at temperatures of 15° to 20°, it has $[a]_D$ $-22 \cdot 12°$. Only four of the molecules of water can be removed by desiccation over sulphuric acid under a reduced pressure in the cold. When heated to 100°, some decomposition of the sparteine takes place. A solution of the salt in water reacts acid to phenolphthalein, and the solution only becomes neutral when sufficient sodium hydroxide solution has been added to combine with one-half the sulphuric acid present in the salt (compare Abstr., 1903, i, 717).

W. P. S.

Methyl and Ethyl Bromides of Alkaloids of the Tropeine and Scopoleine Groups. EMANUEL MERCK (D.R.-P. 145996).—The alkaloids of the tropeine and scopoleine groups combine with alkyl bromides when dissolved in alcohol or chloroform, yielding well-crystallised derivatives. *Hyoscyamine methobromide* forms colourless crystals melting at 210—212° and dissolving readily in water, sparingly in cold alcohol, insoluble in ether. *Atropine methobromide* crystallises from alcohol in white, glistening scales and melts at 222—223°; the *ethyl* compound dissolves in alcohol or water and melts at 173—174°. *Homatropine methobromide* forms colourless crystals and melts at 180—181°. *Scopolamine methobromide* crystallises from ether-alcohol in white needles and melts and decomposes at 216—217°. C. H. D.

Preparation of Chlorotheophylline. C. F. BOEHRINGER & SÖHNE (D.R.-P. 145880).—Chlorocaffeine reacts with phosphorus pentachloride dissolved in phosphorus oxychloride at 100°, or with chlorine in nitrobenzene solution at 50°, forming 1′ : 2-*dichlorocaffeine*,

$$\begin{array}{l} NMe{\cdot}CO{\cdot}C{\cdot}N(CH_2Cl) \\ \vert \qquad\quad \Vert \qquad\qquad\qquad > C{\cdot}Cl, \\ CO{\cdot}NMe{\cdot}C\text{———————}N \end{array}$$

which crystallises from methyl alcohol in groups of long needles and melts at 145°. Warming with water or dilute acids or alkalis hydrolyses it to formaldehyde, hydrogen chloride, and 2-chloro-4 : 6-dimethylxanthine (chlorotheophylline, compare E. Fischer, Abstr., 1895, i, 12), which yields theophylline on reduction. C. H. D.

Transformation of 2-Methylpyrrolidine into 2-Methylpyrrole. GIUSEPPE TESTONI and LUIGI MASCARELLI (*Gazzetta*, 1903, **33**, 267—269).—When 2-methylpyrrolidine is distilled over heated zinc dust, it is converted into 2-methylpyrrole ; the latter was identified by its acetyl and cinnamyl derivatives. W. A. D.

Pyrrole Derivatives. ANGELO ANGELI, FRANCESCO ANGELICO, and ENRICO CALVELLO (*Gazzetta*, 1903, **33**, 270—272. Compare Abstr., 1901, i, 747 ; ii, 381).—The sodium salts of nitroso-derivatives of indoles and pyrroles with an alkyl group in position 2 but with position 3 open, are readily obtained by the action of amyl nitrite and sodium ethoxide. When to the sodium salt of 3-nitroso-2 : 4-dimethylpyrrole, $N{<}\begin{array}{l}CH{=}CMe \\ CMe{\cdot}C{:}N{\cdot}ONa\end{array}$, in aqueous solution, covered with a layer of ether, dilute sulphuric acid is added, the ether becomes coloured with a beautiful but fugitive green tinge, showing that the nitroso-pyrrole set free assumes for a time the true nitroso-structure, $NH{<}\begin{array}{l}CH{=}CMe \\ CMe{:}C{\cdot}NO\end{array}$. On the other hand, nitrosophenylindole and nitrosotriphenylpyrrole set free from their salts by carbonic or acetic acid are coloured yellow.

Nitrosoindoles are not acted on by hydroxylamine, but nitroso-pyrroles are decomposed ; thus the sodium salt of 3-nitroso-2 : 5-dimethylpyrrole gives the *trioxime*,

$$OH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}C(N{\cdot}OH){\cdot}CMe{:}N{\cdot}OH,$$

which yields a tribenzoyl derivative.

Another difference between nitrosoindoles and nitrosopyrroles is that the former on oxidation readily give nitro-compounds, but the latter undergo a complex change. Pyrrole, however, interacts with ethyl nitrate in presence of sodium forming a yellowish-brown crystalline powder, which dissolves in water and gives precipitates with salts of the heavy metals ; this powder, when dried, is stable in a vacuum, but spontaneously inflames in the air. It is probably the sodium salt of a *pyrrolenitronic acid*, $N{<}\begin{array}{l}CH{:}CH \\ CH{\cdot}C{:}NO{\cdot}OH\end{array}$.

W. A. D.

Action of Bromosuccinic and Dibromosuccinic Acids on the Pyridine and Quinoline Bases. Louis Dubreuil (*Compt. rend.*, 1903, **137**, 1063—1065).—Bromosuccinic acid reacts with pyridine, quinoline, and quinaldine in alcoholic solution to form *pyridine hydrogen fumarate* melting at 193°, *quinoline hydrogen fumarate* melting at 153°, and *quinaldine fumarate* melting at 104° respectively. All these salts crystallise in white needles. In aqueous solution, pyridine gives pyridine hydrogen fumarate; quinoline yields *quinoline hydrogen malate* melting at 151°; whilst quinaldine unites directly with the acid forming *quinaldine bromosuccinate* melting at 57°, which is a very unstable salt breaking down into a mixture of quinaldine fumarate and bromide by merely dissolving in warm alcohol. Dibromosuccinic acid in alcoholic solution gives *pyridine hydrogen dibromosuccinate* melting at 137° with pyridine, *quinoline dibromosuccinate* melting at 108° with quinoline, and *quinaldine hydrogen dibromosuccinate* melting at 133° with quinaldine. The nature of the salt formed is independent of the relative proportions of the acid and base employed.

In aqueous solution, pyridine reacts with dibromosuccinic acid to form (1) *pyridine hydrogen bromofumarate* decomposing at 200°, (2) *pyridine hydrogen acetylenedicarboxylate* decomposing at 210°; quinoline gives under the same conditions *quinoline hydrogen acetylenedicarboxylate* decomposing at 210°, whilst quinaldine yields *quinaldine hydrogen bromomaleate* melting at 130°. M. A. W.

The Piperidylcarbamides. Bouchetal de la Roche (*Bull. Soc. chim.*, 1904, [iii], **31**, 21—24).—The piperidylcarbamides can be obtained by heating piperidine with carbamide or its substitution products. Piperidylcarbamide melts at 93°; m-*chlorophenylpiperidylcarbamide* forms colourless plates melting at 149·5°, soluble in alcohol, ether, or chloroform, sparingly so in benzene; p-*chlorophenylpiperidylcarbamide* forms colourless needles melting at 173—174°, soluble in hot alcohol, chloroform, acetic acid; m-*bromophenylpiperidylcarbamide* forms colourless plates which melt at 157°; p-*bromophenylpiperidylcarbamide* melts at 188°; 1:2:5-*nitrotolylpiperidylcarbamide* forms small, pale yellow needles melting at 152°. Chlorine and bromine act on phenylpiperidylcarbamide giving *trichlorophenylpiperidylcarbamide*, which volatilises at 275—280° without melting, and *tribromophenylpiperidylcarbamide*, which sublimes about 260°. Sulphuric acid attacks these symmetrical carbamides with evolution of carbon dioxide, giving a sulphonated amine; the action of nitric acid is similar. Reducing agents do not attack a piperidylcarbamide unless it contains a nitro-group, whilst boiling alcoholic or aqueous alkali hydroxides are without action.

S. S.

Action of Ethyl Ethoxymethyleneacetoacetate on Monoalkylcyanoacetamides. Giorgio Errera and L. Labate (*Gazzetta*, 1903, **33**, ii, 161—170).—The compound previously obtained by Errera (Abstr., 1902, i, 117) by the interaction of ethyl α-ethoxymethyleneacetoacetate and methylcyanoacetamide, and then described as ethyl ϵ-cyano-δ-ethoxy-β-hexanone-ϵ-carboxylamide-γ-carboxylate, is

probably *ethyl 5-cyano-2-hydroxy-4-ethoxy-6-keto-2 : 5-dimethylpiperidine-3-carboxylate*, $\begin{array}{l}CO{-}CMe(CN){\cdot}CH{\cdot}OEt \\ NH{\cdot}CMe(OH){\cdot}CH{\cdot}CO_2Et\end{array}$, for it reacts neither with hydroxylamine nor phenylhydrazine, and its methyl derivative, when treated with concentrated hydrochloric acid, yields 6-hydroxy-2 : 5-dimethylpyridine-3-carboxylic acid.

The interaction of propylcyanoacetamide, sodium ethoxide, and ethyl ethoxymethyleneacetoacetate yields *ethyl 5-cyano-2-hydroxy-4-ethoxy-6-keto-2-methyl-5-propylpiperidine-6-carboxylate*,

$$\begin{array}{l}CO{-}CPr(CN){\cdot}CH{\cdot}OEt \\ NH{\cdot}CMe(OH){\cdot}CH{\cdot}CO_2Et\end{array}$$

or *ethyl ε-cyano-δ-ethoxy-β-octanone-ε-carboxylamide-γ carboxylate*,

$$CH_3{\cdot}CO{\cdot}CH(CO_2Et){\cdot}CH(OEt){\cdot}CPr(CN){\cdot}CO{\cdot}NH_2,$$

which crystallises from aqueous alcohol in silvery plates melting at 260°. On boiling with hydrochloric acid, it yields *ethyl 6-hydroxy-5-propyl-2-methylpyridine-3-carboxylate*, $C_{12}H_{17}O_3N$, which crystallises from alcohol in shining needles melting at 152°. 6-*Hydroxy-5-propyl-2-methylpyridine-3-carboxylic acid*, $C_{10}H_{13}O_3N$, is deposited from alcohol in slender needles melting and decomposing at about 300°.

Ethyl 5-cyano-2-hydroxy-4-ethoxy-6-keto-2-methyl-5-ethylpyridine-3-carboxylate or *ethyl ε-cyano-δ-ethoxy-β-heptanone-ε-carboxylamido-γ-carboxylate*, $C_{14}H_{22}O_5N_2$, prepared from ethylcyanoacetamide, crystallises in colourless needles melting at 198°.

Ethyl 6-hydroxy-5-ethyl-2-methylpyridine-3-carboxylate, $C_{11}H_{15}O_3N$, crystallises from alcohol in short needles melting at 190°, and the corresponding *acid*, $C_9H_{11}O_3N$, in needles melting and decomposing at 305°.

Ethyl 6-methoxy-2 : 5-dimethylpyridine-3-carboxylate, $C_{11}H_{15}O_3N$, is deposited from aqueous solution in white needles or from benzine in silky needles containing H_2O, which is lost at 70°, the anhydrous compound then melting at 80°; it is readily soluble in methyl or ethyl alcohol.

6-*Methoxy-2 : 5-dimethylpyridine-3-carboxylic acid*, $C_9H_{12}O_3N$, crystallises from alcohol or benzine in needles melting at 167—168°.

T. H. P.

2-Methylindole. CARL RENZ and K. LOEW (*Ber.*, 1903, 36, 4326—4330).—The following compounds of the type

$$CHR(C{<}^{CMe}_{C_6H_4}{>}NH)_2$$

were prepared by condensing 2-methylindole with various aldehydes; the figures in brackets denote the temperature and time of condensation.

The *compound*, $C_{21}H_{22}N_2$, from propaldehyde (100°, 5 hours) crystallises from alcohol in lustrous prisms and melts at 180°. That from *iso*butaldehyde, $C_{22}H_{24}N_2$ (100°, 6 hours), separates from acetone in prismatic plates and melts at 207°. The *derivative*, $C_{23}H_{20}ON_2$, from furfuraldehyde (100°, 6 hours), forms small prisms melting at 220°. From tolualdehyde (120—130°, 6 hours), the *compound* $C_{26}H_{24}N_2$ is obtained; it crystallises from alcohol in tetragonal prisms and melts

at 217—218°. From *o*- and *p*-nitrobenzaldehydes (130—140°, 5 hours), isomeric *compounds*, $C_{25}H_{21}O_2N_3$, are obtained, melting respectively at 230° and 233°. With salicylaldehyde (130—140°, 5 hours), 2-methylindole gives the *compound* $C_{25}H_{22}ON_2$, which crystallises from acetone in white plates and melts at 230—231°. Anisaldehyde (120—130°, 5 hours) gives the *substance* $C_{26}H_{24}ON_2$, forms white needles, and melts at 211—212°; whilst from cinnamaldehyde (110°, 6 hours) the crystalline *compound*, $C_{27}H_{24}N_2$, is obtained, melting at 206°. Cuminaldehyde gives the *derivative* $C_{28}H_{28}N_2$, which separates from alcohol in large, white crystals and melts at 218—219°, and piperonal the *compound* $C_{26}H_{22}O_2N_2$, crystallising from aqueous acetone in leaflets and melting at 213°. W. A. D.

Derivatives of 7-Hydroxyquinoline. CARL BÜLOW and GOTTHOLD ISSLER (*Ber.*, 1903, 36, 4013—4019. Compare Abstr., 1903, i, 718).—*Acetylacetone*-m-*hydroxyanilide*, $OH\cdot C_6H_4\cdot N:CMe\cdot CH:CMe\cdot OH$, crystallises from alcohol in colourless flakes, melts at 135°, and is hydrolysed by alkalis into *m*-aminophenol, acetone, and acetic acid. By the action of hydrogen chloride on a solution of the anilide in acetic acid, it is converted into 7-*hydroxy*-2 : 4-*dimethylquinoline*, $C_{11}H_{11}ON$, which crystallises from alcohol in white needles and melts at 218°; the *hydrochloride* crystallises from alcoholic hydrochloric acid in orange-coloured needles.

Dibenzoylmethane-m-*hydroxyanilide*, $OH\cdot C_6H_4\cdot N:CPh\cdot CH:CPh\cdot OH$, crystallises from alcohol in yellow needles and melts at 172°.

7-*Hydroxy*-2 : 4-*diphenylquinoline*, $C_{21}H_{15}ON$, crystallises from alcohol in long, white, silky, felted needles, and melts at 272°.

Propionylacetophenone-m-*hydroxyanilide*,

$$OH\cdot C_6H_4\cdot N:CEt\cdot CH:CPh\cdot OH,$$

crystallises from alcohol in yellow prisms and melts at 139°.

7-*Hydroxy*-4-*phenyl*-2-*ethylquinoline*, $C_{17}H_{15}ON$, crystallises from alcohol in yellow needles and melts at 251°.

Butyrylacetophenone-m-*hydroxyanilide*,

$$HO\cdot C_6H_4\cdot N:CPr^{\alpha}\cdot CH:CPh\cdot OH,$$

crystallises from alcohol in yellow, rhombic tablets and melts at 152°.

7-*Hydroxy*-4-*phenyl*-2-*propylquinoline*, $C_{18}H_{17}ON$, crystallises from alcohol in minute, white needles and melts at 221°. T. M. L.

Condensations of Cinnamaldehyde and Protocatechualdehyde. CARL RENZ and K. LOEW (*Ber.*, 1903, 36, 4330—4332).—When molecular quantities of cinnamaldehyde and quinaldine are heated for 6 hours at 150°, the *compound*, $C_{19}H_{15}N$, is formed by elimination of $1H_2O$; it crystallises from alcohol in lustrous, prismatic, bright yellow leaflets and melts at 117°. The similar *compound*, $C_{17}H_{13}O_2N$, prepared from protocatechualdehyde and quinaldine crystallises from alcohol, melts at 249°, and gives a *hydrochloride*, $C_{17}H_{13}O_2N,HCl,H_2O$, which forms felted, reddish-yellow needles and melts at 295°. The *compound* formed by condensing protocatechualdehyde and lepidine was isolated as the crystalline *hydrochloride*, $C_{17}H_{13}O_2N,HCl$, which sinters at 234° and melts at 245°; the *platinichloride* darkens at 210° and melts at 215°. W. A. D.

Oxidation of Substituted *o*-Phenylenediamines. FRITZ ULLMANN and FERD. MAUTHNER (*Ber.*, 1903, **36**, 4026—4034. Compare Abstr., 1903, i, 199).—The preparation of phenazine derivatives by oxidation of *o*-phenylenediamine may be extended to substituted *o*-diamines. 4-Chloro-*o*-phenylenediamine is best prepared by nitrating *p*-chloroacetanilide and reducing the nitro-compound with stannous chloride. As the base has been little investigated, some derivatives were prepared. The *sulphate* forms colourless leaflets, dissolving sparingly in cold, readily in hot water or alcohol. 4-*Chloro*-1 : 2-*diacetylaminobenzene* crystallises from toluene in colourless leaflets and melts and decomposes at about 201°, forming 4-*chloromethylbenziminazole*, $C_8H_7N_2Cl$, leaflets melting at 199° and dissolving readily in alcohol or ether, sparingly in benzene. Nitrous acid converts the diamine into 4-*chloroaziminobenzene*, $C_6H_4N_3Cl$, which separates from xylene in colourless crystals and melts at 156°, dissolving readily in alcohol or ether, less readily in toluene. Chlorophenylenediamine combines with phenanthraquinone in acetic acid solution, forming *phenanthrachlorophenazine*, $C_{20}H_{11}N_2Cl$, crystallising from nitrobenzene in greenish-yellow leaflets and melting at 246°, almost insoluble in alcohol and ether, dissolving in concentrated sulphuric acid to a red solution.

Ferric chloride in acetic acid solution oxidises the chlorodiamine at the ordinary temperature to 7-*chloro*-2 : 3-*diaminophenazine*,

$$C_6H_4Cl<\overset{N}{\underset{N}{|}}>C_6H_3(NH_2)_2,$$

which crystallises from boiling aniline in yellowish-brown needles, does not melt at 360°, and dissolves in glacial acetic acid to a red solution. The *hydrochloride* and *nitrate* form brown needles and show a slight green fluorescence in alcoholic solution.

When the oxidation is performed in hydrochloric acid solution, the principal product is 7-*chloro*-2-*amino*-3-*hydroxyphenazine*,

$$C_6H_4Cl<\overset{N}{\underset{N}{|}}>C_6H_3(NH_2)\cdot OH,$$

separating from boiling alcohol, in which it is very sparingly soluble, in small, yellow needles, and dissolving in alkalis to yellow solutions. The *hydrochloride* and *nitrate* form brown needles.

Both phenazines combine with *o*-phenylenediamine hydrochloride on heating in fused benzoic acid at 250° to form 2-*chlorohomofluorindine*, $C_{18}H_{11}N_4Cl$, crystallising from nitrobenzene in greenish-blue needles and dissolving in alcohol to a violet solution with red fluorescence, and in sulphuric acid to a blue solution. The *hydrochloride* forms blue needles, insoluble in water, sparingly soluble in alcohol.

7-Chloro-2-amino-3-hydroxyphenazine combines with chloro-*o*-phenylenediamine to form 2 : 10-*dichlorohomofluorindine*, $C_{18}H_{10}N_4Cl_2$, the solutions of which are greener in shade than those of the monochloro-compound.

Ferric chloride oxidises 4-bromo-*o*-phenylenediamine to 7-*bromo*-2 : 3-*diaminophenazine* and 7-*bromo*-2-*amino*-3-*hydroxyphenazine*, which resemble the corresponding chloro-compounds.

3 : 4-Diaminobenzoic acid, prepared from 3-nitro-*p*-acetotoluide by

oxidation with calcium permanganate, hydrolysis, and reduction with sodium hydroxide and aluminium, is oxidised by ferric chloride, forming brown crystals of *2-amino-3-hydroxyphenazinecarboxylic acid*, dissolving in alkalis to yellowish-red solutions. The carboxyl group is not eliminated on heating. *o*-Phenylenediamine hydrochloride in presence of benzoic acid forms *homofluorindine-2-carboxylic acid*, $C_{19}H_{12}O_2N_4$, blue crystals, dissolving in dilute alkali hydroxides to reddish-violet solutions, and in concentrated sulphuric acid to a cornflower-blue solution. The same acid is obtained on heating 2 : 3-diaminophenazine with 3 : 4-diaminobenzoic acid and benzoic acid at 240—250°.

o-Phenylenediamine-4-sulphonic acid could not be oxidised to an azine derivative, but reacts when its hydrochloride is heated with 2 : 3-diaminophenazine and water at 150—160°, forming blue crystals with bronze lustre of *homofluorindine-2-sulphonic acid*, dissolving in ammonia to a red solution, appearing violet in a thin layer.

C. H. D.

Transformation of Benzidine. ARNOLD F. HOLLEMAN and J. POTTER VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 262—267. Compare Abstr., 1903, i, 249).—Hydrazobenzene was separated as a snow-white substance which turns faintly yellow on exposure to air. The respective influences of the concentration of the acid, the solvent, the particular acid used, and the temperature, on the transformation of hydrazobenzene into benzidine have been studied.

The velocity of the transformation is expressed by the equation $dC_b/dt = KC^2_{HCl}$, where C_b is the concentration of the benzidine formed, C_{HCl} the concentration of the hydrochloric acid at any moment, t the time in minutes, and K the reaction constant.

A. McK.

Reduction of 2-Nitronaphthalene. JAKOB MEISENHEIMER and KLAUS WITTE (*Ber.*, 1903, 36, 4153—4164).—A 30—35 per cent. yield of 2-nitronaphthalene may be obtained from β-naphthylamine by Sandmeyer's method (Abstr., 1887, 720) if a larger excess of acid is used during the process of diazotising, and if the mixture is left for a longer time in contact with the cuprous oxide mixture. When an alcoholic solution of the nitro-compound is boiled with aqueous sodium hydroxide and zinc dust and then air drawn through the solution, a mixture of 2 : 2-azonaphthalene melting at 208° (compare Hantzsch and Schmiedel, Abstr., 1897, i, 185), 2 : 2-diamino-1 : 1-dinaphthyl, 1 : 1-dinaphtha-2 : 2-*o*-diazine, and β-naphthylamine is obtained. The mixture is treated with concentrated hydrochloric acid, when the azo-compound remains undissolved; on the addition of water to the filtrate, the diazine is precipitated, and the addition of ammonia to the second filtrate yields the diaminodinaphthyl.

When 2 : 2-azonaphthalene is reduced by boiling for 2 to 3 minutes with alcohol, sodium hydroxide, and zinc dust, the chief product is *2 : 2-hydrazonaphthalene*, $C_{10}H_7 \cdot NH \cdot NH \cdot C_{10}H_7$, which crystallises in faintly red plates melting at 140—141°. It dissolves readily in most

organic solvents, and the solutions in contact with atmospheric oxygen readily yield azonaphthalene.

Mineral acids readily transform the hydrazo-compound into the isomeric 2 : 2-*diamino*-1 : 1-*dinaphthyl*, $NH_2\cdot C_{10}H_6\cdot C_{10}H_6\cdot NH_2$; prolonged boiling with alkalis also produces the same transformation, and the same compound is formed when azonaphthalene is reduced with zinc dust and acetic acid. It crystallises in colourless needles, melts at 191°, and is readily soluble in most organic solvents, but only sparingly so in methyl or ethyl alcohol. The *hydrochloride*, $C_{20}H_{16}N_2,2HCl$, forms long, colourless needles which, when heated at 240—250° for 5 minutes, yields 1 : 1-dinaphtho-2 : 2-imine (Walder, Abstr., 1883, 208).

1 : 1-*Dinaphtha*-2 : 2-*o-diazine*, $\begin{matrix} C_{10}H_6\cdot N \\ | \quad\quad || \\ C_{10}H_6\cdot N \end{matrix}$, crystallises from alcohol in large, hard needles melting at 267—268°, is only sparingly soluble in the usual organic solvents, but dissolves readily in concentrated hydrochloric acid. The *hydrochloride* forms red needles which gradually lose hydrogen chloride; the *platinichloride*, $(C_{20}H_{12}N_2)_2.H_2PtCl_6$, forms yellowish-red needles. The diazine is not readily reduced by zinc dust and alkali or by stannous chloride, but with zinc dust and acetic acid yields 2 : 2-diamino-1 : 1-dinaphthyl.

When 2-nitronaphthalene is reduced with sodium stannite solution, it yields 2 : 2-azoxynapbthalene and 1 : 1-dinaphtha-2 : 2-*o*-diazine oxide. 2 : 2-*Azoxynaphthalene*, $ON_2(C_{10}H_7)_2$, is soluble in ether and crystallises in small, yellow needles melting at 167—168° to a deep red liquid ; on reduction with zinc dust and alkali, it yields azonaphthalene.

1:1-*Dinaphtha*-2:2-*o-diazine oxide*, $O\!<\!\begin{matrix} N\cdot C_{10}H_6 \\ | \quad\quad | \\ N\cdot C_{10}H_6 \end{matrix}$, is insoluble in ether, crystallises in pale yellow needles, melts and decomposes at 247—248°, is sparingly soluble in most solvents, and on reduction yields dinaphtha-*o*-diazine. J. J. S.

Decomposition of Phenylhydrazones. II. Otto Anselmino (*Ber.*, 1903, 36, 3974—3975. Compare Abstr., 1903, i, 367).—*p*-Hydroxybenzaldehydephenylhydrazone, unlike the ortho-compound, does not yield *p*-cyanophenol and aniline when heated ; the distillate contains only a small amount of aniline and none of the cyanophenol. The acetylphenylhydrazone gives acetanilide, but the second product could not be isolated. The diacetylphenylhydrazone, however, gives acetanilide and the acetylated cyanophenol melting at 57°.

p-*Hydroxybenzaldehydeacetylphenylhydrazone*, crystallises from alcohol in short needles and melts at 182°. The *diacetyl* compound crystallises from a mixture of light petroleum and benzene and melts at 148°. T. M. L.

Lactose Phenylosazone. Charles Porcher (*Bull. Soc. chim.*, 1903, [iii], 29, 1225—1227. Compare Fischer, Abstr., 1885, 53).—The phenylosazone of lactose is unstable and loses water even when dried at atmospheric temperatures, forming an anhydride, which is sparingly soluble in acetone and melts at 223—224°. This change, it

is suggested, accounts for the variety of melting points ascribed to lactose phenylosazone, since the latter becomes more or less dehydrated according to the rate and method of heating adopted in determining this constant. T. A. H.

Preparation of 4 : 5-Diamino-2 : 6-dihydroxypyrimidine. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 144761).—Diacetylaminouracil (diacetylaminodihydroxypyrimidine) is hydrolysed by gentle boiling with a concentrated solution of sodium hydroxide. Both acetyl groups are removed, forming 4 : 5-*diamino*-2 : 6-*dihydroxypyrimidine*, $\begin{matrix} NH\cdot CO\cdot C\cdot NH_2 \\ | \qquad\qquad \| \\ CO\cdot NH\cdot C\cdot NH_2 \end{matrix}$, which may be isolated in the form of its sparingly soluble *sulphate*, $C_4H_6O_2N_4,H_2SO_4,1\frac{1}{2}H_2O$. The formyl derivative (Traube, Abstr., 1900, i, 416) is not hydrolysable by this process, inasmuch as the ring closes forming xanthine. C. H. D.

Benziminazoles. OTTO FISCHER and WALTER HESS (*Ber.*, 1903, 36, 3967—3974).—6-*Nitro*-1-*methylbenziminazole methiodide*,

$$NO_2\cdot C_6H_3<\overset{NMe}{\underset{N}{}}\!\!>CH,CH_3I,$$

crystallises from methyl alcohol in yellow prisms and melts at 259°. The *periodide*, $C_9H_{10}O_2N_3I_3$, forms dark brown crystals. Alkalis convert the methiodide into 6-*nitro*-1 : 3-*dimethylbenziminazolol*, $NO_2\cdot C_6H_3<\begin{matrix}NMe\\NMe\end{matrix}>CH\cdot OH$, which crystallises from dilute alcohol in yellow flakes, melts at 128°, is hydrolysed to formic acid and *m*-nitro-*o*-phenyldimethyldiamine, and can be prepared by heating the latter with glacial formic acid. When the diamine is heated with acetic acid and acetic anhydride it yields 6-*nitro*-1 : 2 : 3-*trimethylbenziminazolol*, $NO_2\cdot C_6H_3<\begin{matrix}NMe\\NMe\end{matrix}>CMe\cdot OH$, which crystallises from dilute alcohol in yellow flakes, melts at 175°, and is hydrolysed to the diamine and acetic acid, though not so readily as the unmethylated compound. The corresponding *iminoazole* separates from hot water in white needles; the *methiodide*, $C_{10}H_{12}O_2N_3I$, separates from dilute methyl alcohol in yellow needles and melts at 267°; the *periodide*, $C_{10}H_{12}O_2N_3I_3$, forms brown needles.

Nitromethylbenziminazole, $C_8H_7O_2N_3$, prepared by nitrating the methylbenziminazole from 1 : 3 : 4-toluylenediamine and formic acid, crystallises from hot benzene in flat tablets and melts at 241°. The *methiodide*, $C_{10}H_{12}O_2N_3I$, of the methylated base crystallises from water in yellow flakes and melts at 238°; the brown *periodide*, $C_{10}H_{12}N_2O_3I_3$, was crystallised from hot methyl alcohol. *Nitro*-1 : 3 : 5-*trimethylbenziminazolol*, $C_{10}H_{13}O_3N_3$, crystallises from dilute alcohol in yellow needles and melts and decomposes at 150°. When hydrolysed, it yields a *nitrotolylenedimethyldiamine*, $C_9H_{13}O_2N_3$, which crystallises from dilute alcohol in scarlet prisms and melts at 194°. The *methiodide* of nitro-1 : 2 : 5-trimethylbenziminazole, $C_{11}H_{14}O_2N_3I$, separates from water in colourless needles and melts at 297°; the *periodide*, $C_{11}H_{14}O_2N_3I_3$, forms long, brownish-red prisms; the *iminazolol*

(carbinol), prepared from the methiodide, crystallises from dilute alcohol in yellow tablets and melts at 195°.

Nitro-4 : 6-dimethylbenziminazole, $C_9H_9O_2N_3$, prepared by nitrating 4 : 6-dimethylbenziminazole, separates from alcohol in white prisms and melts at 268°. On methylation, it gives the *methiodide*, $C_{11}H_{14}O_2N_3I$, which crystallises from alcohol in colourless needles and melts at 214°; the *periodide*, $C_{11}H_{14}O_2N_3I_3$, is also produced. The *carbinol*, $C_{11}H_{15}O_2N_3$, from the methiodide, crystallises from alcohol in glistening, orange-red prisms, melts at 163°, and is not hydrolysed by alkalis, although there is produced a certain amount of *nitroxylenyldimethylcarbamide*, $C_{11}H_{13}O_3N_3$, which crystallises from dilute alcohol in lemon-yellow needles and melts at 132°. T. M. L.

Preparation of Alkylated 4-Amino-1-phenyl-2 : 3-dimethyl-5-pyrazolones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145603).—4-Bromo-1-phenyl-2 : 3-dimethyl-5-pyrazolone reacts with secondary amines, the bromine atom being replaced by the NR_2 group. The chloro- and iodo-derivatives react differently, the halogen atom being replaced by hydrogen.

Dimethylamine reacts in aqueous solution at 150° in a closed vessel, forming the 4-dimethylamino-derivative. Methylethylamine forms *4-methylethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone*, which crystallises from water in leaflets melting at 92°, dissolving easily in alcohol or ether, less readily in water or light petroleum. *4-Piperidino-1-phenyl-2 : 3-dimethyl-5-pyrazolone* crystallises from alcohol in needles and melts at 145°. C. H. D.

Constitution of Rosaniline and Pararosaniline. WALTER L. JENNINGS (*Ber.*, 1903, **36**, 4022—4026. Compare Baeyer and Villiger, Abstr., 1903, i, 811).—Several authors have obtained an amorphous, red precipitate by the addition of sodium hydroxide to a cooled solution of magenta, giving figures on analysis lying between those required by the carbinol and by the anhydride formula.

*Anhydro-*p*-triaminodiphenyltolylcarbinol*, $C_{20}H_{19}N_3$, prepared by heating rosaniline, previously purified by crystallisation from boiling sodium hydroxide solution, at 200° for 2 hours in a current of dry hydrogen, forms a dark red, amorphous mass, insoluble in water and most organic solvents, but dissolving readily in acetone and rather less readily in methyl alcohol. Hydrochloric acid reconverts it into rosaniline hydrochloride.

*Anhydro-*p*-triaminotriphenylcarbinol*, $C_{19}H_{17}N_3$, prepared in the same maner from pararosaniline, is also amorphous, and is converted into pararosaniline hydrochloride by hydrochloric acid. The formation of these anhydrides confirms the quinonoid character of magenta and paramagenta. C. H. D.

Preparation of Triphenylmethane Dyes from Magnesium Dimethylaminophenyl Bromide as a Lecture Experiment. PAUL EHRLICH and FRANZ SACHS (*Ber.*, 1903, **36**, 4296—4299).—No action occurs when magnesium is added to a solution of bromodimethylaniline in absolute ether. The Grignard reaction does, however, take place under the following conditions. Magnesium

powder is covered with absolute ether and ethyl bromide then added. After the ensuing vigorous action is moderated by cooling the mixture, the liquid is decanted and an ethereal solution of bromodimethylaniline added to the magnesium, which is apparently rendered active in this manner so that action ensues with the formation of magnesium dimethylaminophenyl bromide. The latter then reacts with Michler's ketone to give a blue product, which, when acidified by acetic acid, gives hexamethyltriaminotriphenylcarbinol, a product identical with methyl violet.

When benzophenone is used instead of Michler's ketone, dimethylaminotriphenylcarbinol is formed. When an ester of an aromatic carboxylic acid, such as ethyl benzoate, is used, malachite-green or an homologue is produced.

The successive introduction of dimethylamino-groupings into the molecule of triphenylcarbinol may easily be illustrated as a lecture experiment. Magnesium dimethylaminophenyl bromide interacts with dimethylaminobenzaldehyde to form a product which, on acidification by acetic acid, yields the hydrol of Michler's ketone,

$$NMe_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4\cdot NMe_2.$$

A. McK.

Formation of Reduced Osotriazoles. HANS EULER and ASTRID EULER (*Ber.*, 1903, 36, 4253—4256).—*Ethyl* 1 : 2-*dihydroxytriazolidine*-4-*acetate*, $\begin{matrix}OH\cdot N\cdot CH_2\\ \vert \\ OH\cdot N\cdot NH\end{matrix}\!>\!C\!:\!CH\cdot CO_2Et$, prepared by reducing the ammonium derivative of ethyl γ-*iso*nitroso-β-nitrosoaminocrotonate (this vol., i, 146) by means of zinc and acetic acid, crystallises in colourless prisms, melts at 70—71°, and is an acid of similar strength to *o*-nitrobenzoic acid; the *potassium* derivative is colourless and readily soluble; the *barium* derivative,

$$(C_6H_{10}O_4N_3)_2Ba,8H_2O,$$

forms soluble, silky needles; the *silver* derivative, $C_6H_{10}O_4N_3Ag$, can be crystallised from alcohol; the *cupric* and *ferric* derivatives were also prepared.

1-*Hydroxytriazoline*-4-*acetic acid*, $\begin{matrix}HO\cdot N\cdot CH_2\\ \vert \\ N=N\end{matrix}\!>\!C\!:\!CH\cdot CO_2H$, prepared by heating the preceding ester with hydrochloric acid, separates from ether in minute, colourless prisms and melts at 184—185°; the *barium* derivative, $C_4H_3O_3N_3Ba,H_2O$, forms sparingly soluble, colourless needles.

T. M. L.

Triazines. LUDWIG WOLFF and HANS LINDENHAYN (*Ber.*, 1903, 36, 4126—4129).—Wolff (Abstr., 1903, i, 205) has described the preparation of acetophenoneazocyanide, $COPh\cdot CH_2\cdot N\!:\!N\cdot CN$, from hydrogen cyanide and diazoacetophenone. When acetophenoneazocyanide is dissolved in concentrated hydrochloric acid, it forms a substance which melts at 95° and is probably the aminochloride,

$$COPh\cdot CH_2\cdot N\!:\!N\cdot CCl_2\cdot NH_2;$$

on crystallisation from alcohol, hydrogen chloride is eliminated and 3-*chloro*-5-*phenyltriazine*, $CPh\!<\!\begin{matrix}CH-N\\ N:CCl\end{matrix}\!>\!N$, is produced; this separates

from alcohol in colourless needles or prisms and melts at 122—123°. It yields 3-hydroxy-5-phenyltriazine (Wolff, *loc. cit.*) when boiled with a dilute aqueous solution of potassium carbonate.

Acetophenoneazothioformamide, $COPh\cdot CH_2\cdot N{:}N\cdot CS\cdot NH_2$, prepared by passing hydrogen sulphide through an aqueous solution of the potassium salt of acetophenoneazocyanide, separates from alcohol in yellow prisms and melts at 170°. It yields *3-thio-5-phenylhydrotriazine*, $CPh{<}^{CH-N}_{NH\cdot CS}{>}N$, when boiled with potassium carbonate solution and then acidified; this separates from alcohol in red needles, melts at 200°, has the properties of a mercaptan, and readily dissolves in alkali carbonates to form bright yellow salts. When boiled with 20 per cent. nitric acid, it forms the *disulphide*, $(C_9H_6N_3)_2S_2$, which crystallises from benzene in yellow prisms and melts at 183°. A. McK.

Compounds with Two and Three Azine Rings. OSCAR HINSBERG and E. SCHWANTES (*Ber.*, 1903, 36, 4039—4050).—The compound obtained by Bladin (Abstr., 1885, 784) by the action of cyanogen on *o*-phenylenediamine is probably 1 : 2-diaminoquinoxaline of the formula $C_6H_4{<}^{N:C\cdot NH_2}_{N:\dot{C}\cdot NH_2}$, and condenses with *o*-quinones, oxalic acid, and α-keto-acids in accordance with this constitution. It reacts with benzil in glacial acetic acid solution, forming *diphenylpyrazinophenazine*, $C_6H_4{<}^{N:C\cdot N:CPh}_{N:\dot{C}\cdot N:\dot{C}Ph}$, which separates from methyl alcohol in red crystals and melts at 235°, dissolving readily in alcohol, acetone, chloroform, or glacial acetic acid, less readily in ether, insoluble in water. The solution in concentrated sulphuric acid is intensely violet, and deposits a red precipitate on dilution.

Hydroxymethylpyrazinophenazine, $C_6H_4{<}^{N:C\cdot N:CMe}_{N:\dot{C}\cdot N:\dot{C}\cdot OH}$, from pyruvic acid, crystallises from dilute acetic acid in small, bright yellow needles melting at above 300° and dissolving readily in acetic acid, sparingly in water or alcohol. The azine dissolves in potassium hydroxide to a colourless solution, and in mineral acids to slightly yellow solutions.

Dihydroxypyrazinophenazine, from diaminoquinoxaline and oxalic acid at 160°, forms yellowish-white crystals melting at above 300°, almost insoluble in water or organic solvents, but dissolving in dilute acids or alkali hydroxides. The *ammonium* salt, $C_{10}H_6O_2N_4,NH_3$ resembles the azine.

Quinoxalophenanthrazine, $C_6H_4{<}^{N:C\cdot N}_{N:\dot{C}\cdot N}{>}C_{14}H_8$, from phenanthraquinone, crystallises from glacial acetic acid in red needles and melts at 200°, dissolving readily in chloroform, sparingly in alcohol, ether, benzene, or acetone. The *hydrochloride* is a black, unstable powder, decomposing in air. Alcoholic ammonium sulphide reduces the base to *dihydroquinoxalophenanthrazine*, $C_6H_4{<}^{N:C\cdot NH}_{N:\dot{C}\cdot NH}{>}C_{14}H_8$, crystal-

lising from glacial acetic acid in small, yellowish-brown needles melting above 300°, and almost insoluble in alcohol, ether, benzene, or chloroform, the traces that dissolve producing a green fluorescence. Potassium dichromate re-oxidises it to the original azine. *Dihydroquinoxalophenanthrazine phenylsulphone*, $C_{22}H_{13}N_4{\cdot}SO_2Ph$, from the azine and benzenesulphinic acid, may be obtained in crystalline form by addition of water to the acetic acid solution, and dissolves very sparingly in alcohol, acetone, benzene, or ether to solutions with yellowish-green fluorescence, more readily in acetic acid or chloroform, and melts at above 300°. With phosphorus pentachloride, 2 : 3-dihydroxynaphthaquinoxaline (Kühling, Abstr., 1891, 1341) yields 2 : 3-*dichloronaphthaquinoxaline*, $C_{10}H_6{<}\begin{matrix}N{:}CCl\\ |\\ N{:}CCl\end{matrix}$, separating from alcohol as a slightly yellow powder melting at 142°, insoluble in water, but dissolving readily in acetic acid or chloroform, and not decomposed by 10 per cent. potassium hydroxide at 100°. When heated at 160° with 1 : 2-naphthylenediamine in a current of carbon dioxide, it forms *dinaphthafluoflavine*, $C_{10}H_6{<}\begin{matrix}N{:}C{\cdot}NH\\ |\\ N{:}C{\cdot}NH\end{matrix}{>}C_{10}H_6$, which crystallises from glacial acetic acid in small, brownish-yellow needles, darkening without melting at about 300°, dissolving very sparingly in alcohol, benzene, or chloroform to slightly fluorescent solutions. Potassium dichromate oxidises it to *naphthaquinoxalonaphthazine*, $C_{10}H_6{<}\begin{matrix}N{:}C{\cdot}N\\ |\\ N{:}C{\cdot}N\end{matrix}{\geqslant}C_{10}H_6$, crystallising from chloroform in intensely red needles and decomposing at about 300°. Stannous chloride or ammoniacal ammonium sulphide reduce it to the flavine. Benzenesulphinic acid forms *dinaphthafluoflavine phenylsulphone*,

$$C_{22}H_{13}N_4{\cdot}SO_2Ph,$$

crystallising from its green fluorescent solution in acetic acid in yellowish-red needles melting above 300°. Potassium dichromate oxidises it to an intensely red compound, probably a sulphonazine.

2 : 3-Dichloronaphthaquinoxaline reacts with *o*-phenylenediamine, forming naphthafluoflavine, $C_6H_4{<}\begin{matrix}N{:}CH{\cdot}NH\\ |\\ N{:}CH{\cdot}NH\end{matrix}{>}C_{10}H_6$ (compare Abstr., 1902, i, 238).

Fluorubine, $C_6H_4{<}\begin{matrix}N{:}C{\cdot}NH{\cdot}C{:}N\\ |\qquad\quad |\\ N{:}C{\cdot}NH{\cdot}C{:}N\end{matrix}{>}C_6H_4$, prepared by heating dichloroquinoxaline with diaminoquinoxaline and decomposition of the hydrochloride formed, is a yellow, crystalline powder, very sparingly soluble in organic solvents, and dissolving both in acids and alkalis to solutions with red fluorescence. Sodium ethoxide precipitates the brown *sodium* salt. The *hydrochloride*, $2C_{16}H_{10}N_6,3HCl$, forms glistening, golden leaflets decomposed by water.

3-*Chloro*-2-*aminonaphthaquinoxaline*, $C_{10}H_6{<}\begin{matrix}N{:}C{\cdot}NH_2\\ |\\ N{:}CCl\end{matrix}$, prepared by heating dichloronaphthaquinoxaline with alcoholic ammonia under pressure, crystallises from glacial acetic acid in long, colourless needles

melting and darkening at 222°. The yellow *hydrochloride* is insoluble in excess of acid.

Dichloroquinoxaline and dry ethylamine at 120° form *diethyldiaminoquinoxaline*, $C_6H_4<\begin{matrix}N:CH\cdot NHEt\\ | \\ N:CH\cdot NHEt\end{matrix}$, crystallising from dilute alcohol in colourless needles and melting at 156°, dissolving readily in most organic solvents, insoluble in water. C. H. D.

Strain-laws of Ring-systems. OSCAR HINSBERG (*Ber.*, 1903, 36, 4051—4054).—Further experiments have been made to test the conclusions as to the stability of azine-rings arrived at by the author (Abstr., 1902, i, 238). Azines containing 5 rings in linear order have not been prepared, and fluorubine, which is a dihydro-compound of such an azine (see preceding abstract), is not oxidisable to the azine, and the latter is therefore unstable, even if capable of existence. The properties of β-naphthacridine and γ-naphthacridine (Strohbach, Abstr., 1902, i, 183), are also shown to confirm the same laws. C. H. D.

A Condensation Product of Indoxylic Acid and Nitrosoantipyrine. HEINRICH BECHHOLD (*Ber.*, 1903, 36, 4131—4135).—When molecular quantities of nitrosoantipyrine and indoxylic acid in alcoholic solution are boiled, the *compound*, $\begin{matrix}NMe\cdot CMe\\ | \\ NPh—CO\end{matrix}>C\cdot N:C<\begin{matrix}CO\\ NH\end{matrix}>C_6H_4$, separates as brown, glistening crystals which melt and decompose at 269° (corr.). Its *picrate* melts and decomposes at 174—176°. Dilute sulphuric acid converts the compound into isatin and aminoantipyrine. A. McK.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. III. Dihydrotetrazines. ROBERT STOLLÉ (*J. pr. Chem.*, 1903, [ii], 68, 464—468. Compare Abstr., 1903, i, 721; this vol., i, 102).—When heated at 180°, butyrylhydrazide yields 80 per cent. of the theoretical amount of 3 : 6-dipropyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine (compare Pellizzari, Abstr., 1897, i, 231; 1899, i, 858; Hantzsch and Silberrad, Abstr., 1900, i, 261). When heated at 200—250°, benzoylhydrazide yields 3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine, dibenzoylhydrazide, 3 : 5-diphenyloxadiazole, and 2 : 5-diphenyl-1 : 3 : 4-triazole. The diphenyltriazole is probably formed by the action of heat on diphenyldihydrotetrazine, as diundecyldihydrotetrazine yields diundecyltriazole on distillation. 1 : 4-Dihydro-1 : 2 : 4 : 5-tetrazine is formed by the action of ethyl orthoformate on hydrazine hydrate at 120°. When shaken with benzaldehyde, it yields a condensation product which melts at 170°. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. IV. Osotetrazines. ROBERT STOLLÉ (*J. pr. Chem.*, 1903, [ii], 68, 469—471. See foregoing abstract).—The action of iodine on the silver derivative of glyoxaldibenzosazone leads to the formation of *s*-diphenyldioxadiazole and of glyoxaldibenzosazone. With the mercuric chloride derivative of benzildibenzosazone, the action of iodine leads to the formation of 2 : 3-*dibenzoyl*-5 : 6-*diphenyl*-2 : 3-*di*-

hydro-1 : 2 : 3 : 4-*tetrazine*. When boiled with aqueous alcoholic hydrochloric acid, the dibenzoyl derivative is partly hydrolysed with formation of *benzoyldiphenyldihydrotetrazine*, which is further hydrolysed to diphenyldihydrotetrazine by prolonged boiling with concentrated acids. The iminohydrogen atom of the monobenzoyl derivative is replaceable by metals.

5 : 6-*Diphenyl*-2 : 3-*dihydro*-1 : 2 : 3 : 4-*tetrazine* yields a *silver* derivative with sodium ethoxide and silver nitrate; with hydrogen chloride in ethereal solution, it forms a *hydrochloride* which is hydrolysed by water. By the action of bromine water, it is converted into nitrogen and tolane dibromide, by the action of nitrous acid or amyl nitrite into diphenylosotriazole. With benzaldehyde, diphenyldihydrotetrazine yields a stable condensation product, $\begin{array}{l}\mathrm{CPh{:}N{\cdot}N} \\ | \qquad\quad | \\ \mathrm{CPh{:}N{\cdot}N}\end{array}\!\!>\mathrm{CHPh}$. From attempts to decompose diphenyldihydrotetrazine by heating with acids, only small quantities of hydrazine have been obtained. G. Y.

Azoxy-compounds. Alfred Wohl [and O. Ahlert] (*Ber.*, 1903, 36, 4139—4143. Compare Abstr., 1901, i, 612).—Phenazine-5:10-oxide is not transformed into hydroxyphenazine when heated with sulphuric acid. At 200°, no change occurs, and at 240—250° phenazine is formed.

Azoxybenzene yields an unstable *dibromide*, $C_{12}H_{10}ON_2Br_2$, which on exposure to the air rapidly gives up bromine. Phenazine 5:10-oxide also yields a brown crystalline *dibromide*, $C_{12}H_8ON_2Br_2$, melting at 132—133° and readily decomposed by alkalis. A *hydrobromide*, $C_{12}H_8ON_2Br_2,HBr$, melting at 212—215°, has also been obtained. The *hydrochloride* of phenazine 5:10-oxide, $C_{12}H_8ON_2,HCl$, crystallises in orange-red needles, and when heated, loses hydrogen chloride and gives the free oxide.

On nitration with sulphuric and nitric acids, the oxide yields a mixture of two *dinitro*-derivatives. The one melts at 269° and is almost insoluble in acetone, the other melts at 240°, and is somewhat more readily soluble in acetone. J. J. S.

Diazo-compounds. Arthur Hantzsch (*Ber.*, 1903, 36, 4361—4366).—Controversial, in reply to Euler (this vol., i, 119). C. H. D.

Isomerism of Diazoxides. Eugen Bamberger (*Ber.*, 1903, 36 4054—4055).—The author's view that normal diazoxides are to be regarded as metallic diazonium salts, $\begin{array}{l}\mathrm{Ar{\cdot}N{:}N} \\ \quad | \\ \quad \mathrm{OM}\end{array}$, and the *iso*diazoxides as metal-substituted diazohydroxides, $\mathrm{Ar{\cdot}N{:}N{\cdot}OM}$, was abandoned on account of the difficulty of regarding a base such as diazonium hydroxide as an acid. This difficulty is now removed by the work of von Zawidcki (Abstr., 1903, i, 801), which shows that the absence of hydrolysis of alkali salts of non-conducting acids occurs not only in the case of pseudo-acids, but also with many amphoteric electrolytes. Diazonium hydroxide is thus to be regarded as an amphoteric electrolyte, capable of forming salts with bases as well as with acids. C. H. D.

Toluene-*p*-diazonium Sulphate and the Action of Sulphuric Acid on *p*-Tolyl Methyl Ether. GELLERT ALLEMAN (*Amer. Chem. J.*, 1904, 31, 24—45. Compare Chamberlain, Abstr., 1897, i, 562; Metcalf, Abstr., 1893, i, 585).—Diazo-*p*-toluene sulphate crystallises in lustrous, white flakes or transparent prisms, and is comparatively stable.

When *p*-methoxytoluene, obtained by the action of methyl alcohol on the diazonium compound, is heated with concentrated sulphuric acid, *p*-methoxytoluene-*m*-sulphonic acid is produced, which crystallises from alcohol in long, colourless, hexagonal prisms, melts at 105—108°, and is very soluble in water; its barium, *sodium*, *potassium*, calcium, *magnesium*, *copper*, *zinc*, and *lead* salts are described. When this acid is fused with potassium hydroxide at a comparatively low temperature, potassium *p*-hydroxytoluene-*m*-sulphonate is formed, whilst at higher temperatures methylcatechol seems to be produced.

By the oxidation of *p*-methoxytoluene-*m*-sulphonamide with potassium permanganate, *p*-methoxy-*m*-sulphaminebenzoic acid is obtained, which crystallises in needles or plates, melts at 276—277°, and is soluble in hot alcohol; its *sodium*, *potassium*, *calcium*, *magnesium*, and barium salts are described. If *p*-methoxy-*m*-sulphaminebenzoic acid is cautiously fused with potassium hydroxide, *p*-hydroxy-*m*-sulphaminebenzoic acid is formed, whilst on prolonged fusion at a high temperature, protocatechuic acid is produced. p-*Hydroxy*-m-*sulphaminebenzoic acid*, $CO_2H\cdot C_6H_3(OH)\cdot SO_2\cdot NH_2$, forms radiating clusters of crystals, melts at 258°, decomposes at about 265°, and is soluble in water or alcohol; its *sodium* and *barium* salts are described. E. G.

Acid Reduction of *o*-Ethoxy- and *m*-Methoxy-azobenzenes. PAUL JACOBSON, GEORG FRANZ, and FRITZ HÖNIGSBERGER (*Ber.*, 1903, 36, 4069—4082).—With the view of determining whether the semidine transformation of hydrazo-compounds takes place more readily in cases where the substituent in the hydrazo-compound is in a position other than the para-, the authors have studied the reduction in acid solution of *o*-ethoxy- and *m*-methoxy-azobenzenes. It is shown that the corresponding benzidine bases are formed in good yields in both cases, whilst the semidine bases are formed either not at all or in very small amounts.

o-*Ethoxyazobenzene*, $N_2Ph\cdot C_6H_4\cdot OEt$, prepared by condensation of nitrosobenzene with *o*-phenetidine, separates from light petroleum in red, monoclinic plates and melts at 43—44°. When reduced by zinc dust in boiling alcoholic alkaline solution, it forms o-*ethoxyhydrazobenzene*, $NHPh\cdot NH\cdot C_6H_4\cdot OEt$, which crystallises from light petroleum in white needles and melts at 66°. When *o*-ethoxyazobenzene is reduced by stannous chloride and hydrochloric acid, 3-ethoxy-4 : 4′-diaminodiphenyl (the commercial "ethoxybenzidine"),

$$NH_2\cdot C_6H_4\cdot C_6H_3(NH_2)\cdot OEt,$$

melting at 139° is obtained. Its solution in hydrochloric acid gives an intense orange-red coloration with ferric chloride, which disappears on the addition of concentrated acid. Its *bis*-o-*hydroxybenzylidene* derivative, $OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4\cdot C_6H_3(OEt)\cdot N\colon CH\cdot C_6H_4\cdot OH$, prepared by allowing an alcoholic solution of *o*-ethoxybenzidine and salicylaldehyde to re-

main at the ordinary temperature for 24 hours, crystallises from benzene in yellow needles and melts at 136—137°. The *bis-p-methoxybenzylidene* derivative, prepared from *o*-ethoxybenzidine and anisaldehyde, separates from a mixture of benzene and light petroleum in microscopic needles and melts at 146—147°. The *bis-p-nitrobenzylidene* derivative, $OEt{\cdot}C_{12}H_7(N{:}CH{\cdot}C_6H_4{\cdot}NO_2)_2$, crystallises from benzene in dark red needles and melts indefinitely at 182—183°. The *bis-cinnamylidene* derivative, $OEt{\cdot}C_{12}H_7(N{:}CH{\cdot}CH{:}CHPh)$, prepared from *o*-ethoxybenzidine and cinnamaldehyde, separates from a mixture of benzene and light petroleum in tiny yellow needles and melts at 167—168°.

When an alcoholic solution of ethoxybenzidine is warmed with phenylcarbimide, *ethoxydiphenylene-bis-phenylthiocarbamide*,

$$OEt{\cdot}C_{12}H_7(NH{\cdot}CS{\cdot}NHPh)_2,$$

is produced; when this is heated with 30 per cent. sulphuric acid at 150°, ethoxybenzidine sulphate is formed.

That the ethoxy-group in the ethoxybenzidine examined is in the *o*-position relatively to the amino-group was proved by diazotising the compound and boiling the product with alcohol, when 3-*ethoxydiphenyl* was formed (compare following abstract); this melts at 34° and boils at 305° under atmospheric pressure.

By the transformation of *o*-ethoxyhydrazobenzene, only one base, namely, *o*-ethoxybenzidine, is formed.

m-*Methoxyazobenzene* (compare following abstracts) was reduced in acid solution by stannous chloride and yielded, as the main product, m-*methoxybenzidine* (2-methoxy-4 : 4′-diaminodiphenyl),

$$C_6H_4NH_2{\cdot}C_6H_3(NH_2){\cdot}OMe,$$

which crystallises from a mixture of benzene and light petroleum in stellate plates and melts at 103—103·3°. The *picrate* of *m*-methoxybenzidine begins to decompose at 200° and melts and decomposes at 220°. Its *bis-p-methoxybenzylidene* derivative crystallises from benzene in yellow needles and melts at 150°. Its *diacetyl* derivative, $OMe{\cdot}C_{12}H_7(NH{\cdot}COMe)_2$, melts and decomposes at 285°.

By the diazotisation of *m*-methoxybenzidine and subsequent action of alcohol, the diazo-groups were apparently replaced not by hydrogen, but by the ethoxy-groups. The elimination of the amino-groups from *m*-methoxybenzidine was successfully accomplished, however, by reducing the diazo-derivative to the corresponding dihydrazine and then oxidising the latter by means of copper sulphate to 2-methoxydiphenyl, melting at 29°.

m-Methoxyhydrazobenzene undergoes benzidine transformation to *m*-methoxybenzidine to the extent of at least from 75—80 per cent. With regard to its semidine transformation, there was no evidence for the formation of a *p*-semidine, but an *o*-semidine was apparently formed to the extent of not more than about 5 per cent. A. McK.

_m_-Compounds of Diphenyl. Constitution of the Diphenyl Bases Derived from _p_-Substituted Hydrazo-compounds. PAUL JACOBSON and ARTHUR LOEB (*Ber.*, 1903, 36, 4082—4093. Compare preceding abstract).—In order to establish the constitution of the ethoxydiphenyl obtained from 4 : 4-diamino-3-ethoxydiphenyl, *m*-hydr-

oxydiphenyl and its ethyl ether have been synthesised by the authors from *m*-nitroaniline.

m-Nitroaniline was diazotised and the potassium *m*-nitro*iso*diazobenzene, obtained by the action of the diazonium solution on a strong solution of potassium hydroxide, was converted into *m-nitrodiphenyl* by means of acetyl chloride and benzene, thus: $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}OK + C_6H_6 + CH_3{\cdot}COCl = NO_2{\cdot}C_6H_4Ph + N_2 + KCl + CH_3{\cdot}CO_2H$. 3-Nitrodiphenyl separates from aqueous alcohol in bright yellow, tetragonal leaflets and melts at 61°. Its constitution was further determined by oxidising it with chromic acid, when *m*-nitrobenzoic acid was produced.

3-*Aminodiphenyl*, $NH_2{\cdot}C_6H_4Ph$, prepared by the reduction of 3-nitrodiphenyl with tin and hydrochloric acid, boils at 176—178° under 18 mm. pressure, and solidifies to stellate groups of needles which melt at 30°. When the diazonium salt is decomposed with water, it forms 3-*hydroxydiphenyl*, $OH{\cdot}C_6H_4Ph$, which crystallises in glistening, white needles melting at 78°.

3-*Ethoxydiphenyl*, prepared by boiling an alcoholic solution of 3-hydroxydiphenyl with sodium ethoxide and ethyl iodide, distils at 160—161° under 9 mm. pressure yielding a colourless oil, which quickly crystallises and then melts at 34—35°. It is identical with the ethoxydiphenyl obtained from 4 : 4-diamino-3-ethoxydiphenyl (compare preceding abstract), and yields *m*-hydroxydiphenyl when heated with hydriodic acid.

Certain *p*-substituted hydrazo-compounds undergo rearrangement in such a manner that the main product is not that of the benzidine transformation, but the amino-compounds produced are primary diamines of the diphenyl series. Those diphenyl bases, $C_{12}H_7R(NH_2)_2$, which are formed from *p*-substituted hydrazo-compounds,

$$R{\cdot}C_6H_4{\cdot}NH{\cdot}NHPh,$$

contain the substituent R in the meta-position relatively to that where the benzene rings join. This view was confirmed by transforming *p*-acetoxyhydrazobenzene into diaminohydroxydiphenyl, removing the amino-groups from the latter, and then converting the product into its ethyl ether, which was found to be identical with 3-ethoxydiphenyl.

Diphenyl bases, formed from *p*-substituted hydrazo-compounds, contain one amino-group, heteronuclear to the substituent R and in the para-position relatively to that where the benzene rings join. This was confirmed by the oxidation of hydroxybisacetylaminodiphenyl to *p*-acetylaminobenzoic acid.

The diphenyl bases in question accordingly contain the amino-groups in the positions 2 : 4′ (diphenyline position). This was proved in the case of chlorodiaminodiphenyl, from which the chlorine was removed by dissolving the base in hot alcohol and then adding an excess of sodium; the resulting product was identified as *iso*benzidine by its conversion into its bis-*o*-hydroxybenzylidene derivative by aid of salicylaldehyde.

The diphenyl bases are therefore constituted thus:

$$[R : NH_2 : NH_2 = 5 : 2 : 4'].$$

*iso*Benzidine may be further characterised by its conversion into *diphenylenedithiocarbimide* (*diphenyl*-2 : 4′-*dithiocarbimide*),

$$C_{12}H_8(N{:}CS)_2,$$

produced by the action of a chloroform solution of thiophosgene on an aqueous solution of *iso*benzidine containing a little hydrochloric acid; this substance separates from light petroleum in needles and melts at 94°. By the action of ammonia, it is converted into *diphenylenebisthiocarbamide* (2 : 4′-*bisthioureidodiphenyl*), $C_{12}H_8(NH\cdot CS\cdot NH_2)_2$, which forms glassy plates melting at 201°.

Diphenylenebisphenylthiocarbamide, $C_{12}H_8(NH\cdot CS\cdot NHPh)_2$, formed from aniline and diphenylenedithiocarbimide, melts at 164°.

A. McK.

m-Hydroxyazobenzene. Constitution of *p*-Hydroxyazo-compounds. PAUL JACOBSON and FRITZ HÖNIGSBERGER (*Ber.*, 1903, 36, 4093—4123).—Although compounds containing the hydroxyl group in the meta-position relatively to the azo-group are known, the simplest type of such *m*-hydroxyazo-compounds, namely, *m*-hydroxyazobenzene, $OH\cdot C_6H_4\cdot N_2\cdot Ph$, had not previously been isolated. The authors have prepared and studied this compound with the particular aim of throwing light on the debated question as to the constitution of *o*- and *p*-hydroxyazo-compounds.

Benzeneazo-o-*anisidine* (2-*amino*-5-*benzeneazoanisole*),

$$N_2Ph\cdot C_6H_3(NH_2)\cdot OMe,$$

prepared by combining *o*-anisidine with diazobenzene, separates from toluene in reddish-brown plates and melts at 110·5—111·5°.

Benzeneazo-o-*phenetidine* (2-*amino*-5-*benzeneazophenetole*),

$$N_2Ph\cdot C_6H_3(NH_2)\cdot OEt,$$

prepared in an analogous manner from *o*-phenetidine, crystallises from light petroleum in orange-yellow needles and melts at 109—110·5°. When acted on by stannous chloride, it undergoes decomposition into aniline and 2 : 5-diaminophenetole, which were identified by the formation from them of benzanilide and 2 : 5-bisbenzaminophenetole (m. p. 213°) (compare succeeding abstract).

Benzeneazo-m-*anisole* (3-*methoxyazobenzene*), $N_2Ph\cdot C_6H_4\cdot OMe$, prepared from benzeneazo-*o*-anisidine by diazotisation and reduction of the diazonium compound by alcohol, boils at 193—193·5° (corr.) under 15 mm. pressure and melts at 32·7—32·8°.

Benzeneazo-m-*phenetole* (3-*ethoxyazobenzene*), $N_2Ph\cdot C_6H_4\cdot OEt$, prepared in an analogous manner by removal of the amino-groups from benzeneazo-*o*-phenetidine, separates from light petroleum in tetragonal plates, melts at 63·5—64°, and boils at about 200° under 22 mm. pressure. Its constitution was further proved by reducing it to the corresponding hydrazo-compound, which, when heated with alcoholic potash and zinc dust at 160°, yields aniline and *m*-phenetidine. The latter was identified by its melting point and by its conversion into *phenyl*-m-*phenetylthiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_6H_4\cdot OEt$, melting at 138·5°.

m-*Hydroxyazobenzene*, $N_2Ph\cdot C_6H_4\cdot OH$, prepared by hydrolysing benzeneazo-*m*-anisole or benzeneazo-*m*-phenetole by aluminium chloride, crystallises from benzene in amber-coloured prismatic rods; it softens at 112° and melts mainly at 112—114° when quickly heated. Its solution in dilute alkalis and in concentrated hydrochloric acid is of

a deep orange-red colour. Its *sodium* salt forms yellow needles; its *acetyl* derivative separates from light petroleum in orange-coloured, glassy plates and melts at 67·5°; its *benzoyl* derivative separates from light petroleum in glistening red plates and melts at 91·5—92°.

m-Hydroxyazobenzene is contrasted with its ortho- and para-isomerides. *m*- and *p*-Hydroxyazobenzene form salts with bases much more readily than does *o*-hydroxyazobenzene. The hydrochlorides of *m*- and *p*-hydroxyazobenzenes are stable, but the hydrochloride of *o*-hydroxyazobenzene is unstable at the ordinary temperature. The hydrochlorides also differ in solubility; the platinichlorides are also contrasted. The cryoscopic behaviour of the meta-compound in naphthalene solution has been studied; its behaviour resembles that of the para-compound, and is different from that of the meta-compound.

m-Hydroxyazobenzene is readily reduced to the corresponding hydrazo-compound, in this respect differing from *o*- and *p*-hydroxyazobenzenes, which yield aniline and the corresponding aminophenols on reduction. m-*Hydroxyhydrazobenzene*, $OH\cdot C_6H_4\cdot NH\cdot NHPh$, prepared by reducing *m*-hydroxyazobenzene by zinc dust and glacial acetic acid, separates from a mixture of benzene and light petroleum in glistening, colourless needles and melts at 126—126·5°. It is an unusual type of hydrazo-compound, since it contains a hydroxyl group, to the presence of which its solubility in water is doubtless due.

m-*Ethoxyhydrazobenzene*, $OEt\cdot C_6H_4\cdot NH\cdot NHPh$, prepared by reduction of *m*-ethoxyazobenzene, crystallises from light petroleum in silky needles and melts at 74—75°.

m-*Hydroxybenzidine* (4 : 4′-*diamino*-2-*hydroxydiphenyl*), prepared by reducing *m*-hydroxyazobenzene in acid solution, crystallises from water in leaflets and melts at 226—227°; it is also readily prepared by the rearrangement of *m*-hydroxyhydrazobenzene; it may also be obtained from *m*-methoxybenzidine by hydrolysing it with hydriodic acid and red phosphorus. Its *bis*-p-*methoxybenzylidene* derivative,

$$OMe\cdot C_6H_4\cdot CH\colon N\cdot C_6H_3(OH)\cdot C_6H_4\cdot N\colon CH\cdot C_6H_4\cdot OMe,$$

prepared from *m*-hydroxybenzidine and anisaldehyde, crystallises from xylene in yellow needles and melts at 200°.

Bisazo-compounds were also prepared from *m*-hydroxyazobenzene, the entrant group, $\cdot N_2R$, taking up a para-position relatively to the hydroxyl group in the original hydroxyazobenzene.

3-*Benzeneazo*-4-p-*bromobenzeneazophenol*,

$$OH\cdot C_6H_3(N_2Ph)\cdot N_2\cdot C_6H_4Br,$$

prepared by diazotising *p*-bromoaniline to form a solution of *p*-bromodiazobenzene and then acting on the latter with an alkaline solution of *m*-hydroxyazobenzene, forms yellow needles and decomposes at about 115°. Its *benzoyl* derivative forms stellate groups of red crystals and melts at 175—176·5°. The constitution of 3-benzeneazo-4-*p*-bromobenzeneazophenol was determined by reducing it to 3 : 4-diaminophenol (compare following abstract).

The bearing of the authors' results on the constitution of hydroxyazo-compounds is discussed and the conclusion drawn that *p*-hydroxyazo-compounds, not only in the form of their metallic salts, alkyl ethers, and acyl derivatives, but also in the free state, are true azo-compounds and are not quinone-hydrazones. This conclusion presupposes the non-

existence of *m*-quinones; it is in opposition to the views advanced by Hantzsch and others. A. McK.

Diaminophenols. PAUL JACOBSON and FRITZ HÖNIGSBERGER (*Ber.*, 1903, 36, 4124—4126. Compare preceding abstract).—2-p-*Methoxybenzylideneamino-5-nitrophenol*,

$$OMe\cdot C_6H_4\cdot CH:N\cdot C_6H_3(NO_2)\cdot OH,$$

prepared by heating molecular amounts of anisaldehyde with 2-amino-5-nitrophenol at 160°, crystallises from benzene in prismatic plates and melts at 160—161°. When sodium ethoxide is slowly added to its alcoholic solution mixed with ethyl bromide, anisaldehyde is eliminated and ethylation takes place with formation of 5-*nitro*-2-*aminophenetole*, $NH_2\cdot C_6H_3(NO_2)\cdot OEt$, which crystallises in yellow needles melting at 91°. On reduction, it yields 2 : 5-diaminophenetole, which was converted into *dibenzoyl*-2 : 5-*diaminophenetole*,

$$C_6H_3(NHBz)_2\cdot OEt,$$

by benzoylation. This separates from aqueous alcohol in asbestos-like needles and melts at 213°.

Dibenzoyl-3 : 4-*diaminophenol benzoate*, $C_6H_3(NHBz)_2\cdot OBz$, prepared by benzoylating the reduction product of 3-nitro-4-aminophenol, separates from alcohol in needles and melts at 225°. When hydrolysed, it forms dibenzoyldiaminophenol, which crystallises in glistening plates, which melt at 203—205°. A. McK.

[β-Naphtholazo-α-naphthol-5-sulphonic Acid.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145906).—The diazonium compounds of 1-chloro-β-naphthylamine-5-sulphonic acid and of β-naphthylamine-1 : 5-disulphonic acid are decomposed by prolonged warming with sodium carbonate, the chlorine atom in the first case and the 1-sulphonic group in the second case being replaced by hydroxyl, forming 2-diazo-α-naphthol-5-sulphonic acid, which combines with β-naphthol to form a brownish-violet dye. C. H. D.

[Azo-compounds from Acyl-*p*-aminophenols.] DAHL & Co. (D.R.-P. 146265).—*p*-Aminophenol does not combine with diazonium salts, but combination is readily produced when the formyl or acetyl derivative is employed in alkaline solution. Azo-compounds were obtained with diazotised naphthionic acid, 4-aminoaceto-α-naphthalide-6-(or 7-)-sulphonic acid, and β-naphthylamine-8-sulphonic acid. *Formyl*-p-*aminophenol* crystallises from water in groups of small needles and melts at 139—140°. C. H. D.

Azo- and Azomethine Derivatives of 2-Aminoanthraquinone. FELIX KAUFLER (*Zeit. Farb. Text.-Chem.*, 1903, 2, 469—473).—2-Aminoanthraquinone is diazotised by converting it into its hydrochloride in glacial acetic acid solution and subsequently adding a 30 per cent. excess of amyl nitrite; it is easily soluble in acetic acid, is precipitated by ether, and is stable at the ordinary temperature. The following compounds were prepared by coupling it with phenols. *Anthraquinone-2-azophenol*, $C_{20}H_{12}O_3N_2$, crystallises from anisole and decomposes at 290°. *Anthraquinone-2-azo-α-naphthol* separates from the same solvent as a red, crystalline mass and melts at about 278°. *Anthraquinone-2-azo-β-naphthol* forms long, scarlet needles and melts at

262—264°. *Anthraquinone-2-azo-β-naphthol-7-sulphonic acid* is moderately soluble in hot water. *Anthraquinone-2-azoresorcinol* separates from glacial acetic acid as a red, crystalline mass and melts and decomposes at 261—263°. *Anthraquinone-2-azosalicylic acid* crystallises from alcohol in a flocculent mass and melts and decomposes at 270°. *Anthraquinone-2-azomethylaniline* and *anthraquinone-2-azodimethylaniline* crystallise from amyl alcohol in needles and melt at 264—266° and 202—204° respectively.

The following compounds were obtained by condensing 2-aminoanthraquinone with aldehydes. *Benzylidene-2-aminoanthraquinone*, $C_6H_4{:}(CO)_2{:}C_6H_3{\cdot}N{:}CHPh$, separates from toluene or anisole in light yellow or brown crystals and melts at 185—187°. o-*Hydroxybenzylidene-2-aminoanthraquinone* forms golden-yellow needles and melts at 229—231°; the analogous p-*derivative* crystallises from nitrobenzene in dark golden-yellow needles melting at 258°. o-, m-, and p-*Nitrobenzylidene-2-aminoanthraquinones* melt respectively at 216—218°, 245—246°, and 246—249°, and vary in colour from yellow to brownish-yellow.

The colour relationship of the foregoing substances is discussed.

W. A. D.

Azo-compound from 3 : 6-Diaminoquinol Dialkyl Ethers and 1 : 8-Dihydroxynaphthalene 3 : 6-disulphonic Acid [" Chromotrope"] Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 146210).—The dialkyl ethers of 3 : 6-diaminoquinol (Nietzki and Rechberg, Abstr., 1890, 967) may be diazotised and then combined with "chromotrope" acid, forming a blue azo-compound, $NH_2{\cdot}C_6H_2(OAlk)_2{\cdot}N{:}N{\cdot}C_{10}H_3(OH)_2(SO_3H)_2$. The same product is obtained on diazotising the acetyl derivative, combining with "chromotrope" acid, and hydrolysing, or by diazotising the nitroamino-ether, combining with the acid, and reducing the nitro-group with sodium sulphide.

C. H. D.

Isomerism of the Salts of Aminoazobenzene. JOHANNES THIELE (*Ber.*, 1903, 36, 3965—3967).—A *red* hydrochloride of aminoazobenzene can be prepared by adding ethereal hydrogen chloride to an ethereal solution of the base; the salt is stable when dry and free from acid, but is converted into the ordinary violet salt by acids, by heating, and by pressure. The red salt also separates when an aqueous solution of the hydrochloride is precipitated by means of sodium chloride.

T. M. L.

Action of Carbon Dioxide on Aqueous Solutions of Aniline in the presence of Nitrites. LOUIS MEUNIER (*Compt. rend.*, 1903, 137, 1264—1266).—Aniline reacts with sodium nitrite in aqueous solution, saturated with carbon dioxide, to form diazoaminobenzene; the reaction proceeds slowly; with silver nitrite under the same conditions, the reaction is much more rapid, and the aniline is converted quantitatively into the silver derivative of diazoaminobenzene, $Ph{\cdot}N_2{\cdot}NPhAg$.

The reaction is explained as follows: the carbon dioxide reacts with the aniline to form aniline carbonate, which undergoes double decom-

position with sodium nitrite to form aniline nitrite, $NH_3Ph\cdot NO_2$; this compound, by the loss of a molecule of water, is transformed into phenylnitrosoamine, $NHPh\cdot NO$, which in its tautomeric *iso*diazo-form $Ph\cdot N\colon N\cdot OH$, condenses with aniline to give diazoaminobenzene, $Ph\cdot N\colon N\cdot NHPh$. The author finds that the formation of diazoaminobenzene by the action of sodium nitrite in a dilute aqueous solution of aniline (compare Niementowski and Rozskowski, Abstr., 1897, i, 340) is to be attributed to the presence of carbon dioxide dissolved in the water, as pure, boiled, distilled water kept from contact of air gives no precipitate with aniline and sodium nitrite even after a month.

M. A. W.

Diazoaminophenols and Hydroxylaminophenols. ALFRED WOHL [and F. GOLDENBERG] (*Ber.*, 1903, 36, 4143—4152).—Free diazoaminophenols may be obtained by hydrolysing their benzoyl esters with cold methyl-alcoholic potassium hydroxide solution in the presence of hydroxylamine.

p-Benzenediazoamino-p-*phenyl benzoate*, $COPh\cdot O\cdot C_6H_4\cdot N_2\cdot NHPh$, obtained by the action of aniline on the chloride of *p*-diazophenyl benzoate, crystallises from methyl alcohol in pale yellow plates melting at 132·5° (corr.) and is readily soluble in most organic solvents. On hydrolysis, it yields p-*hydroxydiazoaminobenzene*, $OH\cdot C_6H_4\cdot N_2\cdot NHPh$, which may be isolated by passing carbon dioxide into the ice cold aqueous solution. It forms yellow crystals, melts at about 80°, is readily soluble in all the ordinary solvents, including water and light petroleum, and is remarkably unstable. With alcoholic hydrogen chloride, it yields aniline and *p*-hydroxybenzenediazonium chloride.

The p-*tolyl* compound, $COPh\cdot O\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4Me$, forms reddish-yellow crystals, melts at 148·5° (corr.) and on hydrolysis yields p-*hydroxybenzenediazo*-p-*aminotoluene*, $OH\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4Me$, which decomposes at 63° (corr.).

The isomeric p-*diazo*-o-*toluidinophenyl benzoate* melts at 131—132° (corr.), but the free hydroxy-derivative is so unstable that it has not been obtained in a pure state.

p-Aminophenol, *m*- and *p*-nitroanilines, and 2:4-dinitroaniline do not react with *p*-diazophenyl benzoate in acetic acid solution. α-Naphthylamine reacts yielding 4-*aminonaphthaleneazo*-p-*phenylbenzoate*,

$$COPh\cdot O\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot NH_2,$$

which crystallises from benzene in orange-coloured needles melting at 183—184° and is insoluble in water or light petroleum. On hydrolysis, it yields 4-hydroxybenzeneazo-4-aminonaphthalene in the form of a red, crystalline powder which sinters at 193° (corr.) and decomposes at 200° (corr.). On reduction and benzoylation, it yields the dibenzoyl derivative, $C_{10}H_6(NH\cdot COPh)_2$ [1 : 4], melting at 280·5° (corr.), and identical with the compound obtained by benzoylating 1 : 4-naphthylenediamine.

The isomeric compound, *αβ-dibenzoylnaphthylhydrazine*,

$$C_{10}H_7\cdot N(COPh)\cdot NH\cdot COPh,$$

obtained by benzoylating naphthylhydrazine, melts at 195—196° (corr.).

p-Nitrophenyl acetate, when reduced with zinc dust and water in the presence of ammonium chloride and benzene, yields p-*azoxyphenyl-*

acetate, $O<\begin{matrix}N\cdot C_6H_4\cdot OAc \\ | \\ N\cdot C_6H_4\cdot OAc\end{matrix}$, in the form of pale orange-coloured, felted needles melting at 169° (corr.) When *p*-nitrophenyl benzoate is reduced in hot alcoholic solution with zinc dust and calcium chloride and then shaken with benzaldehyde, *benzylidene-*p*-hydroxylaminophenyl benzoate*, $O<\begin{matrix}CHPh \\ | \\ N\cdot C_6H_4\cdot O\cdot COPh\end{matrix}$, melting at 205°, is obtained.

*Benzylidene-*p*-aminophenyl benzoate*, $COPh\cdot O\cdot C_6H_4\cdot N:CHPh$, melts at 148° (corr.). J. J. S.

Composition of Gelatin Rendered Insoluble by Chromium Salts and the Theory of the Action of Light on Gelatin in Presence of Chromates. Part I. AUGUSTE LUMIÈRE LOUIS LUMIÈRE and ALPHONSE SEYEWITZ (*Bull. Soc. chim.*, 1903, [iii], 29, 1077—1088. Compare Abstr., 1903, ii, 150).—The precipitation of solutions of gelatin is brought about by many chromic salts and the insolubility of the product in boiling water is most marked in the case of the least acid salts, such as the basic chromic sulphate, $Cr_2(SO_4)_2$ (Recoura, Abstr., 1891, 1430). Precipitation of the gelatin is independent of the nature of the acid radicle of the salt used. No precipitation occurs when solutions of chromium sesquioxide in alkalis are added to solutions of gelatin, but if chromium hydroxide is precipitated in solutions of gelatin, the insoluble gelatin compound is formed unless alkali is added in excess. It was found that 2 grams of chrome alum is the minimum quantity which can be added to 100 grams of gelatin to give a precipitate resistant to boiling water, whilst the maximum amount of the salt which can be absorbed by 100 grams of gelatin is about 21 grams. Chrome alum appears to be absorbed as such by gelatin, but sulphuric acid can be slowly washed out of the insoluble product so formed by boiling water, whence it is probable that the combination occurs between chromium sesquioxide and gelatin. This view is supported by the fact that the ash left on incineration of the precipitate, however prepared, consists only of the oxide.

The gelatin compound, when freshly precipitated, is an elastic, transparent mass having the colour of the salt used in producing it; when washed, it becomes translucent and finally opaque (this form can be obtained at once by the addition of excess of chrome alum to a solution of gelatin in dilute ammonia). When dried, it becomes green in colour and brittle. In this state it contains 3·3 to 3·5 grams of chromium sesquioxide for every 100 grams of gelatin. Both acids and alkalis decompose it, reproducing soluble gelatin.

T. A. H.

Digestion of Casein by Pepsin Hydrochloric Acid and by Pancreas-ferment. EMIL FISCHER and EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1903, 45, 215—219. Compare Abstr., 1903, ii, 666). —In addition to the polypeptide previously mentioned, small amounts of α-pyrrolidinecarboxylic acid are also formed by the prolonged action of pepsin hydrochloric acid or of pancreatin on casein. Its formation has been proved by its isolation without the aid of the esterification method. The best yield is obtained when the proteid is first digested

with the pepsin solution and then for some time with pancreatin. Phenylalanine is also formed. The polypeptide has an alkaline action; its alkaline solution gives a reddish-purple coloration with a very little dilute cupric sulphate solution; it yields a precipitate with tannin and also with platinic chloride and alcohol. J. J. S.

Variations in the Action of Pepsin on Fibrin in Acid Liquids at 50°. Disdier (*J. Pharm. Chim.*, 1903, [vi], 18, 594—605).—It is shown that the digestive power of pepsin diminishes with the time during which it is warmed at 50° with hydrochloric acid (containing 1·5 grams per litre) before the fibrin is added. Syntonisation and peptonisation are found to be most rapid with the 1·5 acid, the former process being, however, equally so with strengths from 1·5 to 2·5 grams per litre. Similar results are obtained with pepsins of an acidic character.

The strengths of hydrobromic, nitric, and sulphuric acids most favourable to the digestive process are found to be almost exactly those equivalent to the 1·5 hydrochloric acid, whilst lactic, oxalic, and formic acids give results different to those obtained with the mineral acids. G. D. L.

Hydrolysis of Edestin. Emil Abderhalden (*Zeit. physiol. Chem.*, 1903, 249—250. Compare Abstr., 1903, i, 588).—The crude leucine obtained from edestin has been found to contain aminovaleric acid. J. J. S.

Salmin. Albrecht Kossel (*Zeit. physiol. Chem.*, 1903, 45, 311—315. Compare Abstr., 1898, i, 714; 1899, i, 833; 1903, i, 303).—Active α-pyrrolidinecarboxylic acid is one of the products obtained by the hydrolysis of salmin with sulphuric acid. The phenylhydantoic acid melted at 137—138°, whereas Fischer (Abstr., 1901, i, 781) gives 143°. J. J. S.

A Phosphorised Constituent of Plant-seeds. Ernst Schulze and Ernst Winterstein (*Zeit. physiol. Chem.*, 1903, 40, 120—122).—The compound previously obtained (Abstr., 1896, i, 516) from the seeds of *Sinapis niger* and other seeds is probably a mixture of Posternak's anhydroxymethylene-phosphoric acid (Abstr., 1903, ii, 680) and some other compound richer in carbon. J. J. S.

The Coagulation of Starch. Jules Wolff and Auguste Fernbach (*Compt. rend.*, 1903, 137, 718—719).—Many cereal grains and leaves contain an enzyme, *amylocoagulase*, which precipitates soluble starch from its solutions. A solution containing 4 to 4·5 per cent. of starch is precipitated by a cold water extract of malt. In more dilute solutions, coagulation may not take place, owing to the antagonistic action of amylase, which, however, is more retarded by the addition of sodium hydroxide than is that of amylocoagulase. The addition of 0·0001 part of acetic acid or sodium hydroxide prevents the reaction, which also disappears after heating the extract at 65° for five minutes.

The coagulative action is not due to the reversed action of an amylolytic ferment, and it is possible that many assumed cases of

reversible enzyme action (compare Croft Hill, Trans., 1903, **83**, 578) may be explicable by the existence of two antagonistic enzymes.

C. H. D.

Enzyme from Monilia Candida and a Milk Sugar Enzyme. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Zeit. physiol. Chem.*, 1903, **45**, 167—175).—When the method used for the extraction of zymase from yeast is applied to *Monilia candida*, an extract is obtained which has strong inverting properties but does not readily induce alcoholic fermentation. A similar preparation may be obtained by treating the organism with acetone (compare Albert, Abstr., 1901, i, 180; 1902, ii, 521). These preparations presumably contain an enzyme resembling zymase. This *monilia-invertase* will not dialyse through parchment paper, may be mixed for a short time with acetone or ether without being destroyed, and will withstand a temperature of 33° for some time, but appears to lose its activity when strongly diluted with water.

The milk sugar yeast from Armenian Mazun also yields an extract which is capable of inducing slight fermentation in a solution of dextrose or milk sugar, owing probably to the presence of a small amount of a zymase in addition to the lactase. The enzymes zymase, monilia-invertase, and yeast lactase resemble one another in certain respects. They only act in the interior of the organism in which they are contained. They can be extracted by the usual method and also remain when the organisms are destroyed by acetone.

J. J. S

Influence of Concentrated Sugar Solutions on Yeast Invertase. THOMAS BOKORNY (*Chem. Zeit.*, 1903, **27**, 1106—1107. Compare Abstr., 1902, i, 848).—The observation made by the author that a syrupy solution of sucrose is not so readily fermented as a similar solution of dextrose led to the conclusion that invertase is affected by concentrated sugar solutions, and to a greater degree than zymase. Invertase in expressed yeast is stable up to 35—40°. The action of invertase on sucrose is very rapid; for instance, a 5 per cent. sugar solution, to which the requisite amount of expressed yeast has been added, reduces Fehling's solution after a few minutes.

Experiments are quoted on the action of expressed yeast on sucrose and dextrose solutions of varying concentrations. The invertase ceases to act on the sucrose solutions when a certain concentration has been reached, whilst the zymase is not affected to the same extent by the increasing concentration of dextrose.

A. McK.

Organic Chemistry.

Preparation and Properties of Symmetrical Dimethylallene. CONSTANT KUKURITSCHKIN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 873—882).—The action of phosphorus pentachloride on trichloroamyl alcohol yields: (1) a *trichloropentylene*, $C_5H_7Cl_3$, to be investigated later, and (2) $\beta\gamma\gamma\delta$-tetrachloropentane. Treatment of the latter with zinc dust in alcoholic solution gives: s-*dimethylallene*,

$$CHMe\!:\!C\!:\!CHMe,$$

which boils at 49—51° and has the sp. gr. 0·7217 at 0°/0° and 0·7024 at 20°/0°. It does not react with an ammoniacal solution of cuprous chloride or with alcoholic silver nitrate. When treated in ethereal solution with sodium, it gives a compound which, when carbon dioxide is passed through the solution, yields Δ^{α}-hexinoic acid: (1) $3CHMe\!:\!C\!:\!CHMe + 2Na = 2CH_3\cdot CH_2\cdot CH_2\cdot C\!:\!CNa + C_5H_{10}$ and (2) $CH_3\cdot CH_2\cdot CH_2\cdot C\!:\!CNa + CO_2 = CH_3\cdot CH_2\cdot CH_2\cdot C\!:\!C\cdot CO_2Na$. With alcoholic potassium hydroxide, it gives Δ^{β}-pentinene, thus: (1) $CHMe\!:\!C\!:\!CHMe + EtOH = CH_2Me\cdot C(OEt)\!:\!CHMe$; (2) this compound then breaks down giving $EtOH + CEt\!:\!CMe$. T. H. P.

Preparation of Primary Alcohols from the Corresponding Amides. LÉON BOUVEAULT and GEORGES BLANC (*Compt. rend.*, 1904, **138**, 148—150).—A solution, made by dissolving the amide in three times its weight of ethyl alcohol, is allowed to flow on to sodium (6 atoms) placed in a flask provided with a long condenser. After the violent reaction is over, the mixture is heated until all the sodium has dissolved. Water is then added and the whole distilled in steam; the mixture of the amine and corresponding alcohol which passes over can be separated by means of acid. The amides of *n*-hexoic, *n*-nonoic, and phenylacetic acids, when subjected to this treatment, furnished *n*-hexyl and *n*-nonyl alcohols and benzylcarbinol respectively. The yields vary between 25 and 30 per cent. of the theoretical. S. S.

A New Method of Synthesising Tertiary Alcohols with Organomagnesium Compounds. VICTOR GRIGNARD (*Compt. rend.*, 1904, **138**, 152—154).—When compounds of the type $R\cdot CO\cdot O\cdot MgX$ are warmed with a magnesium alkyl haloid, the following reactions take place: $RCO\cdot OMgX + R'MgX = CRR'(OMgX)_2$, $CRR'(OMgX)_2 + R'MgX = CRR'_2\cdot OMgX + O(MgX)_2$. By decomposing the product with ice, acidifying, and extracting with ether, a tertiary alcohol can be isolated in good yield. The following new alcohols were prepared by this method. *Diethyl*iso*amylcarbinol*, a mobile liquid of agreeable odour, boiling at 83—86° under 15 mm pressure, having the sp. gr. 0·852 at 0°, 0·844 at 10·4°/4°, and $n_D = 1·44092$; the *acetate* boils at 93—94° under 14 mm. pressure. iso*Butyldi*iso*amylcarbinol* is an oily liquid which boils at 126—129° under 15 mm. pressure, has the

sp. gr. 0·8498 at 0°, 0·8416 at 10·4°/4°, and n_D 1·44864. *Phenyldiethylcarbinol*, a mobile liquid which boils at 101—102° under 11 mm. pressure, has the sp. gr. 1·0029 at 0°, 0·9936 at 11°/4°, and n_D = 1·52672. S. S.

Addition of Hypochlorous Acid to Allene Hydrocarbons. I. F. W. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 854—872).—When two molecules of hypochlorous acid combine with one of allene or of an unsymmetrically substituted allene, the chief products are chlorinated keto-alcohols, which have distinctive properties and may be employed for characterising the allene hydrocarbons.

Chloroacetylcarbinol (*a-hydroxy-γ-chloroacetone*), $CH_2Cl{\cdot}CO{\cdot}CH_2{\cdot}OH$, obtained in about 40—50 per cent. yield by the action of hypochlorous acid on allene, separates from alcohol in crystals melting at 74—75°; it is readily decomposable and, at its melting point, evolves hydrogen chloride; it reduces Fehling's solution at the ordinary temperature, gives a crystalline compound with sodium hydrogen sulphite, and yields the corresponding acetyl compound with acetic anhydride; the action of hydroxylamine on its decomposition products gives methylglyoxime. Other compounds obtained by the action of hypochlorous acid on allene are *s*-dichloroacetone, β-chloroallyl alcohol, and ββ-dichloropropylene glycol.

The action of hypochlorous acid on allene hence takes place in the following different ways: (1) $CH_2{:}C{:}CH_2 + HClO = CH_2{:}CCl{\cdot}CH_2{\cdot}OH$, and then (*a*) $CH_2{:}CCl{\cdot}CH_2{\cdot}OH + HClO = CH_2Cl{\cdot}CCl(OH){\cdot}CH_2{\cdot}OH = CH_2Cl{\cdot}CO{\cdot}CH_2{\cdot}OH + HCl$ and (*b*) $CH_2{:}CCl{\cdot}CH_2{\cdot}OH + HClO = OH{\cdot}CH_2{\cdot}CCl_2{\cdot}CH_2{\cdot}OH$, (2) $CH_2{:}C{:}CH_2 + 2HClO = CH_2Cl{\cdot}CO{\cdot}CH_2Cl + H_2O$.

The dichloropropylene glycol is formed only in very small amount. T. H. P.

Transformations of Octyl *ditert*-γ-Glycol (γ-Tetramethylbutyleneglycol). S. POGORŽELSKY (*J. Russ. Phys. Chem. Soc.*, 882—896).—This compound, βε-dimethylhexane-βε-diol,

$$OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OH,$$

previously obtained by Zelinsky (Abstr., 1902, i, 593), was prepared by the action of magnesium methiodide on ethyl succinate and is found to melt at 88·5—89° and not at 92—93° as stated by Zelinsky (*loc. cit.*).

The action of aqueous sulphuric acid (of strengths varying from 10 per cent. acid to a mixture of 3 vols. of acid and 2 of water) on the glycol yields the corresponding oxide, $\begin{matrix}CH_2{\cdot}CMe_2\\ | \\ CH_2{\cdot}CMe_2\end{matrix}\!\!>\!O$, which is also obtained by the action of hydrochloric acid on the glycol. By treating the glycol with acetic acid at temperatures up to 100°, the monoacetyl derivative is obtained together with a small proportion of the diacetyl compound; but with concentrated acetic acid in a sealed tube at 125° the glycol yields this oxide. In all cases it is supposed that with acetic acid the monoacetyl derivative is obtained, but that at higher temperatures (above 100°), this splits up into the oxide and acetic acid; probably a

similar action takes place when the glycol is heated with sulphuric or hydrochloric acid. The glycol is not acted on by aqueous potassium hydroxide, either at the ordinary temperature or when heated in a water-bath.

The action of potassium hydroxide solution on di*iso*crotyl bromide varies with the temperature. In all cases, however, the first change is the same, namely: $CMe_2Br\cdot CH_2\cdot CH_2\cdot CMe_2Br + H_2O = OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CMe_2Br + HBr$. If the temperature is higher than 77°, the compound thus formed splits up giving the corresponding oxide and hydrogen bromide, whilst at lower temperatures it takes up water and gives the glycol and hydrogen bromide. T. H. P.

Etherates of Haloid Compounds of Magnesium. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 610—623).—The author has determined the solubilities in ether at different temperatures of the compounds $MgBr_2,2Et_2O$ and $MgI_2,2Et_2O$ (see Tissier and Grignard, Abstr., 1901, i, 316; and Zelinsky, Abstr., 1903, i, 802), to which he gives the name of "dietherates." Two non-miscible liquid layers are formed, from the lower of which the dietherate is obtained on cooling. The dietherate of magnesium bromide melts under ether at 22·8°. Complete miscibility of the two layers of liquid was found to be unattainable, owing to decomposition occurring before a sufficiently high temperature was reached. This dietherate may melt under ether at higher temperatures than 22·8°. For this to take place, it is necessary that the quantity of ether in contact with the solid dietherate be less than is contained in the lower liquid layer at 22·8°. The content of dietherate in the solution then increases to 85·5 per cent. at 30°, but with greater concentrations, that is, when still less ether is taken, the dietherate decomposes into monoetherate and ether.

With the magnesium iodide compound, two liquid layers are obtained with ether, the melting point of the compound under ether being 23·6°; the critical solution temperature is 38·5°. The pure magnesium iodide dietherate melts at 51·5°. T. H. P.

The Phosphoric Esters of Glycerol. P. CARRÉ (*Compt. rend.*, 1904, **138**, 47—49. Compare this vol., i, 133).—A description of the properties of the three glyceryl phosphates which are obtained by the action of glycerol on phosphoric acid. Glyceryl dihydrogen phosphate (glycerophosphoric acid), $PO(OH_2)\cdot O\cdot C_3H_5(OH)_2$, is best obtained by decomposing an aqueous suspension of the lead salt with hydrogen sulphide, and concentrating the filtrate from the lead sulphide under reduced pressure; it forms an uncrystallisable syrup. It is impossible to obtain it quite pure and free from water, for, at a certain concentration (2 mols. acid, 1 mol. water), it begins to change to the diphosphate. Glyceryl hydrogen phosphate, $OH\cdot PO{<}{\scriptstyle\begin{matrix}O\cdot CH_2\\O\cdot CH_2\end{matrix}}{>}CH\cdot OH$, was not isolated; in aqueous solution, it readily decomposes giving the monophosphate. Glyceryl phosphate, $PO\vdots O_3\vdots C_3H_5$, was obtained as a spongy mass, insoluble in water and alcohol. S. S.

Esterification by means of Sulphuric Acid. HANS MEYER (*Monatsh.*, 1903, **24**, 840—843).—In the ordinary method of esterification by means of sulphuric acid, an excess of alcohol is employed, and only the minimum quantity of mineral acid is added. It is often advantageous to dissolve the acid in concentrated sulphuric acid and to add an equivalent quantity of the alcohol. After stirring, the solution is poured on to crystallised sodium carbonate, neutralisation thus occurring without development of heat. Mixed anhydrides or acylsulphuric acids, $R \cdot CO \cdot SO_4H$, are first formed and then react with the alcohol forming the ester. The method gives good results with acids of the pyridine series and with most fatty and aromatic acids. No esterification occurs in the case of *p*-hydroxybenzoic acid or terephthalic acid, the *p*-substituent apparently hindering the formation of acylsulphuric acids (compare Abstr., 1901, i, 628).

C. H. D.

The Theory of Saponification. LUIGI BALBIANO (*Ber.*, 1904, **37**, 155—157. Compare Abstr., 1903, i, 547, and Lewkowitsch, this vol., i, 6).—In the benzoylation of glycerol by Baumann's method, the product, even when only a few drops of benzoyl chloride have been added, is pure tribenzoin; the esterification, therefore, takes place in the three hydroxyl groups simultaneously and not in stages.

C. H. D.

Salts of Antimony with Organic Acids. I. EDUARD JORDIS (*Zeit. angew. Chem.*, 1904, **17**, 41—45. Compare Abstr., 1902, i, 740; 1903, ii, 603).—A theoretical paper. A. McK.

α-Iodopropionic Acid. WLADIMIR ZERNOFF (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 962—964).—α-Iodopropionic acid, which has previously been obtained only in the form of an impure, non-crystallisable syrup, may be prepared (1) by heating propionic acid (1 mol.), phosphorus pentachloride ($1\frac{1}{4}$ mols.), and chloroform (2 mols.) together at 65°, and gradually adding iodine chloride until the colour of iodine appears in the liquid, the products of the reaction being then decomposed by means of ice-cold water and shaken with sodium carbonate solution; after removal of the chloroform, an oil remains which solidifies in the desiccator to acicular crystals, melting, after recrystallisation from light petroleum, at 44·5—45·5°. (2) By treating ethyl α-bromopropionate in alcoholic solution with potassium iodide and hydrolysing the ester thus obtained with cold barium hydroxide solution. The acid is readily soluble in most organic solvents, but only slightly so in light petroleum or water. Its *lithium* ($+H_2O$), *magnesium* ($+4\frac{1}{2}H_2O$), *barium* and *copper* salts were prepared. Most of its salts are extremely readily soluble in water. T. H. P.

Action of Nitrogen Peroxide on Acids of the Series $C_nH_{2n-2}O_2$. IV. Action of Nitrogen Peroxide on Allylacetic Acid, its Ethyl Ester, and on Propylideneacetic Acid and its Ethyl Ester. IWAN W. EGOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 965—973. Compare Abstr., 1903, i, 789 and 790).—The

action of nitrogen peroxide on an ice-cold light petroleum solution of ethyl allylacetate yields a yellow oil which analysis and cryoscopic examination show to be a mixture of mononitro-derivative, $C_7H_{12}O_2(NO_2)\cdot OH$, and the dinitro-compound, $C_7H_{12}N_2O_6$. The oil is soluble in alkali, to which it imparts a red colour, and on heating it decomposes with evolution of brown vapours. Reduction with tin and hydrochloric acid yields a product from which platinic chloride separates the *platinichloride* of *ethyl γδ-diaminovalerate*,

$$NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO_2Et,H_2PtCl_6.$$

With allylacetic acid, under similar conditions, a small quantity of succinic acid is obtained, together with a mixture of the $NO_2\cdot ONO$ and $NO_2\cdot OH$ compounds, and possibly also the $NO_2\cdot NO_2$ derivative. Reduction of this mixture with tin and hydrochloric acid and treatment of the resulting product with platinic chloride gives the *platinichloride* of *γδ-diaminovaleric acid*, $NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO_2H,H_2PtCl_6$. Free diaminovaleric acid could only be obtained in small quantity from its compound with phosphotungstic acid. Aminovaleric acid, which is also probably formed in the above reduction, could not be separated.

Treatment of propylideneacetic acid and its ethyl ester with nitrogen peroxide yields corresponding mixtures of dinitro- and hydroxy-nitro-derivatives, which gradually decompose with separation of oxalic and propionic acids. Reduction with tin and hydrochloric acid yields a *hydroxyamino-acid*, $OH\cdot C_5H_8O_2\cdot NH_2$, which separates in crystals containing H_2O and melting at about 125°. T. H. P.

Action of Nitrogen Peroxide on Acids of the Series $C_nH_{2n-2}O_2$. V. Action of Nitrogen Peroxide on Oleic and Elaidic Acids. IWAN W. EGOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 973—997. Compare Abstr., 1903, i, 789 and 790, and preceding abstract).—It was shown by Varrentrapp (*Annalen*, 1840, 35, 196) and by Hermann Meyer (*Annalen*, 1840, 35) that nitrous acid gives additive products with oleic acid, and also converts it into elaidic acid. Lidoff (*J. Russ. Phys. Chem. Soc.*, 1895, 27, 117) found that nitrogen peroxide in the cold converts oleic acid into its isomeride, whilst at 80—85° it forms additive products.

The author finds that small quantities of nitrogen peroxide act on oleic acid giving an additive product, and it is only when this latter is present in a certain proportion, for the formation of which a certain minimum quantity of nitrogen peroxide is required, that the isomeric change of oleic into elaidic acid can take place. The action of still larger quantities of nitrogen peroxide on an ice-cold light petroleum solution of oleic acid yields: (1) a crystalline product which proves to be the *nitrous ester* of *nitrohydroxystearic acid*, $NO_2\cdot C_{18}H_{34}O_2\cdot O\cdot NO$, and which crystallises from alcohol in large, thin plates melting at 85—87°, and soluble in ether or ethyl acetate; it has the normal molecular weight in freezing acetic acid, and on keeping it gives up nitrogen and oxygen. With acetic anhydride, it gives the *acetyl* derivative of *nitrohydroxystearic acid*, $OAc\cdot C_{18}H_{34}O_2\cdot NO_2$, as a pale yellow oil, which, when treated with potassium hydroxide, yields nitrohydroxystearic acid,

$OAc\cdot C_{18}H_{34}O_2\cdot NO_2 + 3KOH =$
$$OH\cdot C_{18}H_{32}O_2K_2\cdot NO_2 + C_2H_3O_2K + 2H_2O.$$
(2) Nitrohydroxystearic acid, in the form of a yellow oil. Reduction of the mixed products of the action of nitrogen peroxide on oleic acid by means of zinc and hydrochloric acid yields stearic acid and its mono- and di-hydroxy-derivatives, together with the hydrochloride of an *aminohydroxystearic acid*, $OH\cdot C_{18}H_{34}O_2\cdot NH_2,HCl$, which crystallises in needles melting at 143—144°; the *barium* salt, $(C_{18}H_{35}O_2)_2Ba$, of this acid was prepared, but the acid separated from it did not give concordant numbers on analysis.

The action of nitrogen peroxide on olive oil yields a mixture of the glycerides of nitrohydroxystearic acid and of its nitrous ester; treatment of this mixture with acetic anhydride gives the glyceride of nitroacetoxystearic acid, $[C_{18}H_{33}O_2(NO_2)\cdot OAc]_3C_3H_5$, in an almost pure condition.

The author sums up the results of his previous researches (*loc. cit.*) and of the present work and draws from them the following conclusions: (1) the first product of the action of nitrogen peroxide on an acid of the series $C_nH_{2n-2}O_2$ is a compound of the composition $NO_2\cdot C_nH_{2n-2}O_2\cdot O\cdot NO$; only when the double linking is far removed from the carboxyl group, and when the molecule contains the grouping, $CH_2{:}C<$, is the formation of a certain quantity of the compound $C_nH_{2n-2}O_2(NO_2)^2$ possible. (2) The action of nitrogen peroxide on esters and glycerides of acids of the series $C_nH_{2n-2}O_2$ is similar to its action on the free acids. (3) It is probable that, when left in the air in presence of moisture, the compound $NO^2\cdot C_nH_{2n-2}O_2\cdot O\cdot NO$ passes into $OH\cdot C_nH_{2n-2}O_2\cdot NO_2$. (4) The method of combination of the groups ONO and NO_2 with the acids $C_nH_{2n-2}O_2$ is similar to that of hydriodic acid with these acids, NO_2 taking the place of iodine, and ONO that of hydrogen. (5) The spontaneous decomposition of the products of the combination of nitrogen peroxide with the unsaturated acids, $C_nH_{2n-2}O_2$, may be used as a means of determining the position of the double linking in the acid. (6) Although the products of the action of nitrogen peroxide on *iso*crotonic acid are identical with those obtained from crotonic acid and the products from oleic identical with those from elaidic acid, the successive steps in the reaction are different in the two cases. (7) The conversion of oleic into elaidic acid requires the presence of a certain minimum quantity of nitrogen peroxide, and is accompanied by the formation of additive products. T. H. P.

aa-Dialkylhydracrylic Acids. EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 110—119. Compare Abstr., 1902, i, 357, and succeeding abstract).—Ethyl bromo*iso*butyrate (40 grams), dry trioxymethylene (14 grams), zinc filings (35 grams), and dry benzene (120 grams) were mixed together and after vigorous action had ceased a further 40 grams of the bromo-ester were added, and the mixture heated on the water-bath for 30 minutes. The product was freed from dissolved zinc and unchanged trioxymethylene by pouring into excess of water, and agitation of the solution of the reaction products in benzene first with dilute sulphuric acid and then with ammonia. The products of the reaction were separated into

three volatile fractions and a non-volatile residue. The first fraction boiled at 84—86° under 16 mm. pressure, and when hydrolysed with potassium hydroxide, dissolved in alcohol, furnished β-hydroxy-αα-dimethylpropionic acid (compare succeeding abstract), but when treated with potassium hydroxide dissolved in water there was formed, in addition to the foregoing acid, di*iso*propyl ketone (the *semicarbazone* crystallises in spangles and melts at 150—151°), whence it was concluded that the first fraction contained ethyl hydroxydimethylpropionate (Abstr., 1902, i, 357) and ethyl *iso*butyrylbutyrate.

The second fraction, which boiled at 110—116° under 18 mm. pressure, consisted principally of ethyl tetramethylsuccinate (compare Brown and Walker, Abstr., 1893, i, 394). The third fraction boiled from 151—160° under 15 mm. pressure and consisted of β-hydroxy-ααγγ-tetramethylglutarate (Abstr., 1898, i, 631). T. A. H.

Hydroxypivalic Acid [β-Hydroxy-αα-dimethylpropionic Acid]. L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 119—130).—[*β-Hydroxy-αα-dimethylpropionic acid*], $OH \cdot CH_2 \cdot CMe_2 \cdot CO_2H$, prepared as described in the preceding abstract, crystallises in clear needles, melts at 124°, is very soluble in water, alcohol, or benzene, less so in ether, and insoluble in light petroleum. Its electric conductivity K is 0·00139, which is slightly higher than that of pivalic acid, – 0·000978. When oxidised by chromic acid in presence of sulphuric acid, it is converted into dimethylmalonic acid. The *calcium, sodium, ammonium,* and *copper* salts are described. The ethyl ester (Abstr., 1902, i, 357) is a colourless liquid with a pleasant odour; it boils at 133° under 40 mm. and at 188° under 750 mm. pressure and has a sp. gr. 0·9985 at 20°/4°. The *methyl* ester boils at 177—178° under 740 mm. pressure and has a sp. gr. 1·0365 at 20°/4°. No amide, anilide, or *p*-toluidide of the acid could be obtained.

Benzylamine hydroxydimethylpropionate crystallises in needles and melts at 108—109°, and, when heated at 200—220° for 3 hours, is converted into the corresponding *benzylamide*; this crystallises in transparent tablets, melts at 64°, and is insoluble in light petroleum. The *phenylhydrazide*, similarly prepared, crystallises from ethyl acetate in yellow-tinted spangles, melts at 173°, and is insoluble in water.

Ethyl β-acetoxydimethylpropionate, $OAc \cdot CH_2 \cdot CMe_2 \cdot CO_2Et$, prepared by acetylating ethyl hydroxypivalate with acetyl chloride, is a liquid of pleasant odour, boils at 94° under 16 mm. pressure, at 202° under 750 mm., and has a sp. gr. 1·0100 at 20°/4°. The *methyl* ester boils at 191—192° under 737 mm. pressure and has a sp. gr. 1·0338 at 20°/4°. The free *acid* crystallises from light petroleum, melts at 56°, and is very soluble in alcohol. The *calcium* salt was prepared.

When ethyl hydroxydimethylpropionate, dissolved in ether, is treated with metallic sodium and ethyl iodide, a mixture of two esters is formed. The more volatile of these consists of *ethyl ethoxydimethylpropionate*, a pleasant-smelling liquid which boils at 75° under 22 mm. pressure, and, on hydrolysis, furnishes *β-ethoxy-αα-dimethylpropionic acid*, which is crystalline and boils at 123° under 22 mm. pressure. The *sodium* salt of this was prepared.

The less volatile ester consists of *ethyl hydroxydimethylpropionyl-*

oxydimethylpropionate, $OH \cdot CH_2 \cdot CMe_2 \cdot CO \cdot O \cdot CH_2 \cdot CMe_2 \cdot CO_2Et$, which distils at 154° under 27 mm. pressure, and, when hydrolysed by potassium hydroxide dissolved in alcohol, furnishes hydroxypivalic acid.

With phenylcarbimide, hydroxydimethylpropionic acid furnishes the corresponding *phenylurethane*, $NHPh \cdot CO \cdot O \cdot CH_2 \cdot CMe_2 \cdot CO_2H$, which crystallises from light petroleum or boiling water and melts at 126°. The *potassium* salt of this is crystalline, melts at 129—130°, and is very soluble in water. T. A. H.

Researches in the Glyceric Acid Series. I. *d*- and *l*-Glyceric Acids. CARL NEUBERG and M. SILBERMANN (*Ber.*, 1904, 37, 339—341).—In a research not yet published, Neuberg and Neimann obtained from *d*-glucuronic acid an optically active glyceric acid, the barium salt of which had $[\alpha]_D$ +17·1°. Frankland and Appleyard (Trans., 1893, 63, 298) find $[\alpha]_D$ −10·1° for the barium salt of the *d*-acid, obtained by the growth of *Bacillus ethaceticus* on calcium *i*-glycerate. The authors have accordingly resolved *i*-glyceric acid into its optically active components by means of brucine, the solvent being ethyl alcohol. The brucine salt, obtained after four crystallisations, was decomposed by baryta water, and the resulting barium salt gave $[\alpha]_D$ −17·38° (c = 7·704) in aqueous solution. The mother liquor, from which the brucine *d*-glycerate had been separated, yielded a barium salt having $[\alpha]_D$ 8·75° (c = 13·71). A. McK.

Researches in the Glyceric Acid Series. II. Conversion of Diaminopropionic Acid into *iso*Serine. CARL NEUBERG and M. SILBERMANN (*Ber.*, 1904, 37, 341—345. Compare preceding abstract and Ellinger, this vol., i, 230).—The transformations undergone by amino-acids are important in connection with the formation of sugars from proteids. Neuberg and Wolff (Abstr., 1903, i, 74) have already shown that *d*-α-amino-*n*-hexoic acid can be obtained from *d*-glucos aminic acid. The replacement of the amino-groupings in αβ-diaminopropionic acid has now been studied.

*iso*Serine was produced by the action of silver nitrite on αβ-diaminopropionic monohydrobromide; it was identified by its copper and phenylcarbimide derivatives (E. Fischer and Leuchs, Abstr., 1903, i, 12).

The *phenylcarbimide* derivative of *αβ-diaminopropionic acid*, prepared from αβ-diaminopropionic hydrochloride, sodium hydroxide solution, and phenylcarbimide, melts and decomposes at 214° (corr.).

A. McK.

Separation of Hydrogen Ions from Methylene Groups. RICHARD EHRENFELD (*Ber.*, 1904, 34, 83—84).—A reply to Wagner and Hildebrandt's criticisms (this vol., i, 140). W. A. D.

Cryoscopic Observations on Solutions of Oxalic Acid in presence of Neutral Salts. A. FEDOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 643—644).—The author has made cryoscopic measurements of (1) solutions of oxalic acid, ammonium chloride, and ammonium oxalate, containing from one-half to one-thirty-second of an

equivalent per litre, and (2) solutions of oxalic acid mixed with those of either ammonium chloride or ammonium oxalate. The first of these salts does not affect the cryoscopic behaviour of oxalic acid, but, when the latter is present, depressions less than the normal are obtained. This the author considers to be due to the formation of acid or complex salts. T. H. P.

Coefficient of Distribution of Oxalic Acid between Water and Ether in presence of Neutral Salts. A. FEDOROFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 639—640).—The concentration of the oxalic acid in the aqueous phase is increased by the addition of sodium or potassium oxalate, but diminished in presence of ammonium chloride. T. H. P.

Asymmetric Synthesis. WILLY MARCKWALD (*Ber.*, 1904, 37, 349—354).—All previous attempts to synthesise an optically active carbon compound, as, for example, Cohen and Whitely (Proc., 1901, 16, 212), Kipping (Proc., 16, 226), and Fischer and Slimmer (Abstr., 1902, i, 621), have been based on the one principle; they have involved the combination of an inactive compound, containing an ethylene linking or a carbonyl group, with an optically active substance to form an ester or glucoside, and the subsequent treatment of this product in such a way as to attach two different groups to a carbon atom previously ethenoid so as to render it asymmetrical. As Japp and others have pointed out, the two possible isomerides should not necessarily be formed in equal quantities, so that one of the isomerides would preponderate on hydrolysing the new ester or glucoside, and therefore an optically active substance should be obtained. The formation in this manner of optically active substances has not yet, however, been conclusively established.

Methylethylmalonic acid, $CMeEt(CO_2H)_2$, forms two acid salts, which, in the case of the potassium salt, are enantiomorphously related and will have the same solubility, whereas the two acid salts with an optically active base will in general have different solubilities. When heated, methylethylmalonic acid loses carbon dioxide, forming α-methylbutyric acid, which contains an asymmetric carbon atom; it is to be supposed that from the acid brucine salts the free carboxyl group will be preferentially eliminated. On heating the brucine salt, crystallised from the mixture of the two in an oil-bath at 170°, a valeric acid was obtained which boiled at 174° and in 100 mm. tube showed α_D $-1{\cdot}7°$, corresponding with 10 per cent. of active *l*-valeric acid. This, after conversion into its silver salt and reconversion into acid (compare Marckwald, 1899, i, 477), showed a rotation α_D $-1{\cdot}2°$ in 50 mm. tube. E. F. A.

General Method for the Preparation of Aldehydes. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1904, 37, 186—188. Compare Bouveault, this vol., i, 13; Gattermann and Maffezolli, *ibid.*, 172).—Aldehydes may be synthesised by the action of organomagnesium haloids on the esters of orthoformic acid dissolved in dry ether. The reaction is only completed when the ether has been distilled off, and the acetal thus

obtained, $CH(OEt)_3 + R\cdot MgI = CHR(OEt)_2 + OEt\cdot Mg\cdot I$, may then be hydrolysed with very dilute acid.

Magnesium ethyl iodide gave a 25 per cent. yield of acetal, magnesium propyl iodide gave 22 per cent. of butaldehyde. The acetal of *iso*valeraldehyde (80), acetal of benzaldehyde (45), acetal of phenylacetaldehyde (62), *p*-bromobenzaldehyde (40), and anisaldehyde (15 per cent.) have been prepared. J. J. S.

Synthesis of Aldehydes. AUGUSTE BÉHAL and SOMMELET (*Compt. rend.*, 1904, **138**, 89—92).—The ethers of α-glycols, corresponding with the formulæ $OH\cdot CR_2\cdot CH_2\cdot OX$ and $OH\cdot CRR_1\cdot CH_2\cdot OX$, in which X represents a univalent alkyl or aromatic residue, are decomposed by heating at 110—115° with dry oxalic acid, yielding substituted aldehydes of the type $CR_2H\cdot CHO$ and $CRR^1H\cdot CHO$, the following scheme representing the probable course of the reaction: $OH\cdot CR_2\cdot CH_2\cdot OX \rightarrow CR_2{:}CH_2\cdot OX \rightarrow CR_2{:}CH_2\cdot OH \rightarrow CR_2H\cdot CHO$.

The α-glycol ethers required for the preparation of the aldehydes, $CR_2H\cdot CHO$, were obtained by Grignard's method (compare Abstr., 1901, i, 250) by the action of ethyl ethoxyacetate on the organo-magnesium derivatives, and the following ethers and aldehydes were prepared: *dimethylethoxymethylcarbinol*, which boils at 129°; *diethylethoxymethylcarbinol*, which boils at 168° and yields *α-ethylbutaldehyde*, which boils at 117—118°; *dipropylethoxymethylcarbinol*, which boils at 201° and yields *α-propylvaleraldehyde*, which boils at 159—161°; *di*iso*butylethoxymethylcarbinol*, which boils at 112—113° under 23 mm. pressure and yields *α-*iso*butyl*iso*hexoaldehyde*, boiling at 185—186°; *di*iso*amylethoxymethylcarbinol*, which boils at 143—144° under 25 mm. pressure and yields *α-*iso*amyl*iso*heptaldehyde*, which boils at 103—105° under 11 mm. pressure; *diallylethoxymethylcarbinol*, which boils at 101—102° under 25 mm. pressure; *diphenylethoxymethylcarbinol*, which boils at 209—210° under 29 mm. pressure and yields *diphenylacetaldehyde*, which boils at 168—170° under 10 mm. pressure; *diethylphenoxymethylcarbinol* boils at 140—142° under 12 mm. pressure and yields α-ethylbutaldehyde when heated with dry oxalic acid.

The α-glycol ethers, required for the formation of the aldehydes, $CRR^1H\cdot CHO$, were obtained by the action of organomagnesium compounds on the ketones $R\cdot CO\cdot CH_2\cdot OEt$, which were prepared by Blaise's method (compare Abstr., 1901, i, 133) from cyanoethoxymethane, $OEt\cdot CH_2\cdot CN$, and the following compounds were prepared. (1) Ketones: *ethoxybutanone*, which boils at 145—146°; *ethoxypentanone*, which boils at 164—165°; *ethoxymethylhexanone*, which boils at 92—93° under 18 mm. pressure, and *ω-ethoxyacetophenone*, which boils at 134—136° under 21 mm. pressure. (2) α-Glycol ethers: *α-ethoxy-β ethylpentan-β-ol*, which boils at 180—184°; *α-ethoxy-ε-methyl-β-propylhexan-β-ol*, which boils at 109—113° under 12 mm. pressure; *α-ethoxy-β-methyloctan-β-ol*, which boils at 110—112° under 14 mm. pressure; *α-ethoxy-β-methylnonan-β-ol*, which boils at 130—133° under 18 mm. pressure. (3) Aldehydes: *α-ethylvaleraldehyde*, which boils at 141—143°; *α-propyl*iso*heptaldehyde*, which boils at 195—198°; *α-methyl-*

octaldehyde, which boils at 92° under 28 mm. pressure, and *α-methylnonaldehyde*, which boils at 98—100° under 20 mm. pressure.

M. A. W.

Compounds of Trichloro- and Tribromo-acetates with Ketones and Aldehydes. L. Koboseff (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 652—667).—By dissolving trichloroacetates or tribromoacetates in ketones and aldehydes, the following compounds have been obtained. All are crystalline, but do not melt sharply, the temperatures given being those at which melting started when the substances were heated in sealed tubes.

With acetone: $(CCl_3{\cdot}CO_2)_2HK,2COMe_2$, needles melting at 39°; $(CCl_3{\cdot}CO_2)_2HK,COMe_2$, melting at 56°; $CCl_3{\cdot}CO_2K,COMe_2$, four-sided prisms decomposing without melting; $4(CCl_3{\cdot}CO_2)_2HNH_4,COMe_2$; $3(CCl_3{\cdot}CO_2)_2HNH_4,COMe_2$.

With methyl ethyl ketone: $(CCl_3{\cdot}CO_2)_2HK,COMeEt$, melting at 55°.

With pinacolin: $(CCl_3{\cdot}CO_2)_2HK,COMe{\cdot}CMe_3$, silky needles melting at 84°; $(CBr_3{\cdot}CO_2)_2HK,Me{\cdot}CO{\cdot}CMe_3$, decomposing without melting.

With acetylacetone: $(CCl_3{\cdot}CO_2)_2HK,COMe{\cdot}CH_2Ac$, rhombic crystals melting at 52°.

With acetophenone: $(CCl_3{\cdot}CO_2)_2HK,COMePh$, melting at 66°.

With benzaldehyde: $(CCl_3{\cdot}CO_2)_2HK,Ph{\cdot}CHO$, melting at 35°; $(CBr_3{\cdot}CO_2)_2HK,Ph{\cdot}CHO$, melting at 88·5°.

With salicylaldehyde: $2(CCl_3{\cdot}CO_2)_2HK,3OH{\cdot}C_6H_4{\cdot}CHO$, melting at 41°; $(CCl_3{\cdot}CO_2)_2HK,2OH{\cdot}C_6H_4{\cdot}CHO$, melting at 38°.

Certain other ketones and aldehydes gave negative results.

These compounds readily effloresce in the air and are decomposed by water. The author regards them not as molecular, but structural compounds, and assigns to them the following constitutions: for neutral salts, $OK{\cdot}CRR^1{\cdot}O{\cdot}CO{\cdot}CCl_3$. For acid salts,

$$OH{\cdot}CRR^1{\cdot}O{\cdot}C(CCl_3)<^{O}_{O}>C(CCl_3)O{\cdot}CRR^1{\cdot}OK \text{ and}$$

$$OH{\cdot}CRR^1{\cdot}O{\cdot}C(CCl_3)<^{O}_{O}>C(CCl_3)O{\cdot}CRR^1{\cdot}OK.$$

T. H. P.

Synthesis of Glucosides. Derivatives of Arabinose. Hugh Ryan and George Ebrill (*Sci. Proc. Roy. Irish. Acad.*, 1903, **24**, B. 303—386. Compare Trans., 1901, 704).—Crystalline acetochloroarabinose is easily prepared by the action of acetyl chloride on arabinose; it reacts with methyl alcohol, forming the methyl arabinoside melting at 166—168°, previously described by Fischer (Abstr., 1894, i, 3). *Carvacryl arabinoside* crystallises from water in long needles melting at 119—120°; *β-naphthyl arabinoside* forms long, branching, grouped needles from alcohol, melting at 176—177°; *o-tolyl arabinoside* crystallises in rosettes melting at 124°. The paper contains a useful summary of previous work on the synthesis of glucosides.

E. F. A.

Some Hydrazones and their Melting Points. A. MÜTHER and BERNHARD TOLLENS (*Ber.*, 1904, 37, 311—315).—*Xylosephenylmethylhydrazone*, $C_5H_{10}O_4{:}N_2MePh$, crystallises from very dilute alcohol, melts at 108—110°, is sparingly soluble in water, but dissolves readily in alcohol and in pyridine; the solution in pyridine showed no optical activity.

l-Arabinosephenylmethylhydrazone melts at 164° and not at 161° (van Ekenstein and Lobry de Bruyn); the diphenylhydrazone melts at 203—205° (Neuberg gives 203—206° for inactive *r*-arabinose, but 216—218° for *l*-arabinose), and has $[\alpha]_D$ + 14·9° in pyridine.

A series of experiments showed that Maquenne's metal block for melting point determinations possesses no advantages over the sulphuric acid flask. T. M. L.

***iso*Rhodeose, the Second Methylpentose from Convolvulin.** EMIL VOTOČEK (*Zeit. Zuckerind. Böhm.*, 1904, 28, 209—212. Compare Abstr., 1903, i, 67).—*iso*Rhodeose yields methylfurfuraldehyde on distillation with 12 per cent. hydrochloric acid, and is hence a methylpentose; it has $[\alpha]_D$ + 20·3°. Its *phenylosazone* and p-*bromophenylosazone*, melting at 183—184°, were prepared, and the former analysed.

The specific rotations of rhodeose and *iso*rhodeose show that the crude syrupy rhodeose consists of a mixture of 1 mol. of rhodeose and 2 mols. of *iso*rhodeose. The crude syrup from convolvulin contains also 1 mol. of dextrose. T. H. P.

Synthesis of Sugars from Trioxymethylene and Sodium Sulphite. ALPHONSE SEYEWETZ and GIBELLO (*Compt. rend.*, 1904, 138, 150—152).—Trioxymethylene (1 part) was dissolved in water (200 parts) containing sodium sulphite (20 parts anhydrous salt) and the mixture boiled; at the end of ten minutes, all odour of formaldehyde had vanished, and the osazones of the sugars formed were precipitated by warming with phenylhydrazine acetate. Examination of the crude osazones revealed the presence of formosazone melting at 148°, and glycerosazone which melted at 131°; another substance was isolated, but has not yet been identified. α-Acrosazone was absent.

S. S.

The Mutarotation of Sugars. E. ROUX (*Ann. Chim. Phys.*, 1903, [vii], 30, 422—432).—By a modification of Muller's method (compare Abstr., 1894, i, 268), the author has redetermined the velocity of transformation of α- into β-glucose, and extended the investigation to the correlated transformation of γ- into β-glucose; he finds that with a unit of time of 30 minutes the velocity of the conversion of α- into β-glucose is practically independent of the concentration, being 1·315 for a 5 per cent. solution, and 1·345 for a 10 per cent. solution at the same temperature, and further that the conversion of γ- into β-glucose proceeds at about the same rate, the velocity being 1·40 for an 8 per cent. solution at 18°. A mixture of α- and γ-glucoses in the proportion of 36·73 : 63·27 has a specific rotatory power equal to that of the β-variety, exhibits no mutarotation, and behaves in fact

like a *racemic* mixture. Similar results were obtained with α- and γ-lactoses, the velocities of conversion of each of these into the β-variety being 1·334 and 1·305 respectively, and a mixture of the two in the proportion of 36·3 : 63·7 acting as a "*racemic* mixture" and having a constant specific rotation equal to that of β-lactose [compare, however, Lowry, Trans., 1899, **75**, 212; 1903, **83**, 1320].

M. A. W.

Melibiose. D. Loiseau (*Zeit. Ver. deut. Zucker-Ind.*, 1903, 1050—1061).—The author has made a very complete study of the properties of pure melibiose prepared from raffinose by fermentation with a top yeast. The sugar crystallises with $2H_2O$ from aqueous or aqueous alcoholic solutions, and is very soluble in cold water and soluble in all proportions in water at 75°. Crystalline melibiose loses its water of crystallisation completely at 120° and the anhydrous sugar absorbs from the air twice the normal quantity of water, half of which is again given up. When first dissolved, hydrated melibiose has a lower specific rotation than the normal, whilst the anhydrous sugar gives at first a higher value; the ultimate normal rotation is 1·926 compared with that of sucrose as unity. If dissolved in presence of an acid or an alkali, melibiose gives the normal rotation immediately; the addition of lead acetate lowers the rotation considerably, but does not precipitate the melibiose. The sugar is only slightly soluble in alcohol, which, in 95 per cent. strength, only dissolves 2—2·4 parts at 15°. Three to 4 parts of melibiose are required to produce the same sweetening effect as 1 part of sucrose.

T. H. P.

Quantity of Non-fermentable Sugar in Sugar Cane Molasses. Henri Pellet and G. Meunier (*Zeit. Ver. deut. Zucker-Ind.*, 1903, **574**, 1182—1185).—Analysis of the molasses from an Egyptian cane-sugar factory gave the following results: H_2O, 26·73; crystallisable sugar, 36·40; dextrose, 6·10; lævulose, 8·48; glutose, 2·40; mannose, 0·20; mineral matter (without CO_2), 8·40, and organic matter, 11·30 per cent. The glutose is quite unfermentable, and so remains in the liquid after fermentation. For the control of the results obtained by the fermentation process, the authors recommend the estimation of the reducing substances before and after inversion by the method given by Pellet (*Bull. de l'Assoc. des Chim. de sucr. et de dist.*, 1898—1899, 1006—1145).

T. H. P.

Products of Hydrolysis of Fucus, Laminaria, and Carragheen Moss. A. Müther and Bernhard Tollens (*Ber.*, 1904, **37**, 298—305).—Seaweed (fucus) was extracted with cold 2 per cent. sulphuric acid, the extract neutralised with calcium carbonate, evaporated under reduced pressure, partially freed from inorganic salts by precipitating with alcohol, further purified by adding sulphuric acid to convert the inorganic salts into sulphates insoluble in alcohol, and neutralising with lead carbonate and hydrogen sulphide, and finally a syrup was obtained which deposited needle-shaped crystals of feebly lævorotatory

mannitol; this was further characterised by condensing with benzaldehyde to Meunier's tribenzylidenemannitol, a compound which melts at 213—214° and not at 207° as described by Meunier. The residue was then hydrolysed by heating on the water-bath during 8 hours with 5 per cent. sulphuric acid; the extract, neutralised with calcium carbonate and freed from mineral salts by the addition of alcohol, gave a precipitate of fucosephenylhydrazone, which was converted into crystalline fucose. After removing the excess of phenylhydrazine by the addition of formaldehyde, diphenylhydrazine was added and arabinosediphenylhydrazone obtained. The syrupy residue was strongly dextrorotatory and appeared to consist of arabinose with a little fucose. A test for xylose by means of bromine and cadmium carbonate gave a negative result, but the presence of *d*-galactose was proved.

Laminaria, examined by a similar method, gave mannitol, fucose, and glucosazone.

Preliminary experiments with carragheen moss gave indications of glucose, galactose, fructose, and pentose groups. Hydrolysis with 2 per cent. sulphuric acid on the water-bath during 5 hours gave a syrup, from which was precipitated the phenylhydrazone of hydroxymethylfurfuraldehyde, whilst extraction with ethyl acetate gave a yellow liquid which showed five of the characteristic reactions of this aldehyde. This aldehyde is known to be an intermediate product in the hydrolysis of fructose to lævulic acid, but it was found to be the chief product even when a much gentler method of hydrolysis was employed. *d*-Galactose was separated as methyl- and benzyl-phenylhydrazones and characterised by its rotatory power and by oxidation to mucic acid. T. M. L.

Fucose and Fuconic Acid and a Comparison with Votoček's Rhodeose and Rhodeonic Acid. A. MÜTHER and BERNHARD TOLLENS (*Ber.*, 1904, 37, 306—311).—*Fucose diphenylhydrazone*, $C_6H_{12}O_4{:}N_2Ph_2$, crystallises from 95—96 per cent. alcohol in colourless needles and melts at 198°. The *phenylmethylhydrazone*, $C_6H_{12}O_4{:}N_2MePh$, crystallises in colourless needles which melt first at 163—164°, but after repeated crystallisation from dilute alcohol at 177°; it closely resembles the preceding compound, but is more soluble; a solution in pyridine gave $[\alpha]_D$ +3·6°. The *phenylbenzylhydrazone*,

$$C_6H_{12}O_4{:}N_2Ph{\cdot}CH_2Ph,$$

was obtained in yellow flakes melting at 161°, but repeated crystallisation gave a colourless product which melted at 172—173°, had $[\alpha]_D$ +9·1°, and resembled in solubility the preceding compound. Attempts to prepare the osazone by means of phenylhydrazine hydrochloride, sodium acetate, and water, and by means of phenylhydrazine acetate gave only the phenylhydrazone.

Fuconic acid was obtained only in the form of its *lactone*, which melts at 106—107°, and gave $[\alpha]_D$ +71·7° and +78·3°. The *potassium*, $C_6H_{11}O_6K,1\frac{1}{2}H_2O$, *barium*, $(C_6H_{11}O_6)_2Ba$, *strontium*, and *calcium*, $(C_6H_{11}O_6)Ca,5H_2O$, salts are described. The *phenylhydrazide*, $C_6H_{11}O_5{\cdot}N_2H_2Ph$, crystallises from hot water in colourless, four-sided flakes and melts at 203—204°.

The following table shows the similarity between fucose and rhodeose and leaves little doubt that they are optical isomerides.

	Fucose.	Rhodeose.
$[\alpha]_D$	$-73°$ to $-75°$	$+73°$ to $+75·2°$
Phenylosazone, m. p.	158° to 159°	176·5°
Phenylhydrazone, m. p.	170° to 172°	172°
Phenylmethylhydrazone, m. p.	177°	174°
Phenylbenzylhydrazone, m. p.	172° to 173°	178° to 179°
Diphenylhydrazone, m. p.	198°	199°
p-Bromophenylhydrazone, m. p.	181° to 184°	184°
	Fuconic.	Rhodeonic.
Lactone, m. p.	106° to 107°	105·5°
Lactone, $[\alpha]_D$	$+73·0°$ to $+78·3°$	$-76·3°$ to $-69·4°$

The only outstanding difference is in the osazone, which is still under investigation; in the case of fucose, the crude product melts at 155—156°, but when purified, yields a product melting at 170—172°, which is, however, not the osazone but the phenylhydrazone.

T. M. L.

Optical Activity of Cellulose and its Nitro-derivatives. Léo Vignon (*Bull. Soc. chim.*, 1904, [iii], 31, 105—108. Compare Levallois, Abstr., 1884, 1288; 1885, 369 and 500; Béchamp, Abstr., 1885, 237; and Vignon, Abstr., 1903, i, 461, 462).—A nitrated cellulose, the composition of which was similar to that required by the formula $C_{24}H_{31}(NO_2)_9O_{21}$, which was soluble in acetone to the extent of 4·5 per cent. and in a mixture of equal volumes of alcohol and ether to the extent of 1·66 per cent., had $[\alpha]_j$ +19·3° in the former solvent ($c = 3·848$ grams in 100 c.c.) and +21·1° when dissolved in a mixture of alcohol and ether ($c = 1·4943$ grams in 100 c.c.).

Thiocellulose, prepared by treating cotton cellulose first with an aqueous solution of sodium hydroxide and then with carbon disulphide vapour in the absence of light, when dissolved in water to the extent of 0·998 per cent. exhibited a slight dextrorotation. T. A. H.

Progress of the Technology of Explosives since the Development of Organic Chemistry. Wilhelm Will (*Ber.*, 1904, 37, 268—298).—A lecture delivered before the German Chemical Society.

Reversion [Transformation] of Starch Paste. Léon Maquenne (*Compt. rend.*, 1903, 137, 1266—1268. Compare Abstr., 1903, i, 679; this vol., i, 17).—In view of Boidin's recent paper on amylocoagulase (compare this vol., i, 276), the author publishes the results already obtained on the influence of alkalis on the reversion of starch paste; he finds that potassium carbonate employed in increasing quantities behaves similarly to the acids, first accelerating, then retarding, and finally preventing the reversion into amylocellulose. The reversion of starch paste, prepared only with pure water and the mineral matters

contained in the raw starch or extracted from the glass vessels, is a progressive reaction in which the starch tends to recover a form closely related to that which it possessed in the natural product. Starch paste is therefore to be regarded as a true colloidal substance, and in the absence of all foreign matter it is not impossible that it would remain unchanged for an indefinite period. M. A. W.

Transformation and Coagulation of Starch Paste. Léon Maquenne, Auguste Fernbach, and Jules Wolff (*Compt. rend.*, 1904, 138, 49—51. Compare Abstr., 1903, i, 679; this vol., i, 17).—The amylocellulose, formed by the spontaneous transformation of starch jelly, does not give a blue colour with iodine until dissolved in a solution of potassium hydroxide; it is not hydrolysed by amylase, and is thus distinguished from the coagulum formed from starch with malt extract. The following method serves to detect amylocellulose which has been produced by spontaneous coagulation. A sample of the starch paste is hydrolysed with excess of malt extract, 10 c.c. of the product are taken out and mixed with 20—25 drops of potassium hydroxide solution of sp. gr. 1·4, and after the lapse of a few minutes acidified with dilute hydrochloric acid. The production of a blue colour with iodine in this solution proves the presence of amylocellulose in the original sample of starch jelly. The spontaneous coagulation of starch proceeds much more slowly than that produced by the action of malt extract. S. S.

Caramel. V. Decomposition Products of Caramelan. Ferdinand Stolle (*Zeit. Ver. deut. Zucker-Ind.*, 1903, 1149—1157. Compare Abstr., 1900, i, 209, and ii, 249; 1901, i, 673).—On hydrolysing caramelan with 3 per cent. sulphuric acid solution, the following products were obtained: (1) 14·64 per cent. (on the weight of caramelan) of a chocolate-brown, humous *substance*, $(C_9H_{11}O_5)_x$, which is insoluble in water, alcohol, acetic acid, or acetone, and on oxidation with nitric acid of sp. gr. 1·15 yields oxalic acid; (2) lævulic acid, and (3) a *hexose* which separates from water in crystals which contain H_2O, and melts at 93°, or from methyl alcohol in an anhydrous form melting at 148° (corr.); it exhibits birotation, the final value of $[\alpha]_D$ for the anhydrous sugar being $+52·60°$; it does not yield a phenylmethylosazone with *as*-phenylmethylhydrazine, and is hence an aldose. Its *phenylosazone* separates in annular aggregates of slender needles, which melts at 201·9° and is decomposed by water; a solution of 0·2282 gram in 25 c.c. of glacial acetic acid has a rotation, $\alpha_D - 1·5°$. On oxidation with nitric acid of sp. gr. 1·15, the sugar yields *d*-tartaric acid, whilst with bromine it gives a pentahydroxyhexoic acid, the *calcium* salt of which, $(C_6H_{11}O_7)_2Ca$, gives a value of $[\alpha]_D$ (+10·99° at 20°) slightly higher than that of calcium gluconate. Fehling's solution is reduced by the hexose to a slightly less extent than by dextrose. It is not decided whether this sugar is identical or stereoisomeric with dextrose.

The amount of copper obtained by the action of caramelan on Fehling's solution varies considerably with the time of heating, but

for 2 minutes' boiling is directly proportional to the amount of caramelan present in the solution.

When heated at 170—180°, sucrose only loses water, according to the equation: $C_{12}H_{22}O_{11} = C_{12}H_{18}O_9 + 2H_2O$; the caramelan thus obtained exhibits normal cryoscopic behaviour in aqueous solution. At a temperature of 190°, sucrose begins to lose carbon dioxide and small quantities of acetone. T. H. P.

Aliphatic Amines. HANS EULER (*Arkiv. Kem. Min. Geol.*, 1903, 1, 67—76; *Annalen*, 1904, 330, 280—289).—In order to decide whether the vinylamine obtained by Gabriel from bromoethylphthalimide is really vinylamine or whether it must be regarded as ethyleneimine, the author has investigated its behaviour and that of methylamine towards nitrous acid. The results show that, although the reaction proceeds with different velocities in the two cases, its course is quite similar for both the bases. Further, it is found that the vinylamine (ethyleneimine) does not react with nitrous acid as do secondary amines, but behaves as follows: (1) 1 mol. of nitrous acid combines with the base forming a nitrite. (2) In the action of 1 mol. of nitrous acid on 1 mol. of the nitrite of the base, either the ring is unopened in the nitrite and then nitrous acid is added on and the ring broken: $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>NH_2{\cdot}ONO \longrightarrow OH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2(NO){\cdot}O{\cdot}NO$, or the nitrous acid reacts with the hydroxyethylamine nitrite already formed with evolution of water, in which case the analogy with the corresponding reaction of methylamine would be complete. Whichever of these two represents the actual course of the reaction, an unstable molecule is formed, and this decomposes according to the equation:

$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}NO,HNO_2 = OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH + N_2 + HNO_2 =$$
$$OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH + N_2 + \tfrac{2}{3}NO + \tfrac{1}{3}HNO_3 + \tfrac{1}{3}H_2O.$$

The results obtained with methylamine show that there is nothing special about the part played by the nitrous acid. The pure nitrite is extremely stable, but when an excess of free nitrous acid is present a much more vigorous evolution of gas occurs than with nitrous acid itself. These facts are explained by assuming that the nitrite and acid combine with loss of water and formation of $NO{\cdot}NH_2Me{\cdot}O{\cdot}NO$, which contains two nitrogen atoms in direct combination; since the basic character of the amine is annulled, or at any rate greatly diminished, by the entry of the NO group into the molecule, the HNO_2 originally in the molecule will be set free.

On the basis of the above representation, the reactions of ammonia and primary, secondary, and tertiary amines with nitrous acid may be explained from a common point of view. In all cases, a hydrogen atom of the nitrite is replaced by NO, by which means a compound is formed containing two nitrogen atoms in direct combination with one another. This nitroso-compound then immediately loses nitrous acid, and shows then a behaviour varying according to the possibilities of its decomposition: with ammonia or a primary amine, the molecule can split up into a hydroxyl compound (water or an alcohol) and nitrogen; in

the case of a secondary amine, the nitroso-compound contains no more hydrogen united to nitrogen and is stable, and with a tertiary amine, assuming the formation of a nitroso-compound, this must be immediately destroyed again, since only N_2O_3, but not HNO_2, can be given up. T. H. P.

Conversion of Diaminopropionic Acid into *iso*Serine. Alexander Ellinger (*Ber.*, 1904, **37**, 335—339. Compare Neuberg and Silbermann this vol., i, 220).—Since the discovery of serine (α-amino-β-hydroxypropionic acid) as a product of the hydrolysis of silk-fibroin (E. Fischer and Skita, Abstr., 1902, i, 654) and of horn (E. Fischer and Dörpinghaus, Abstr., 1903, i, 216), the importance of aminohydroxy-aliphatic acids has been emphasised.

By the action of silver nitrite on an aqueous solution of αβ-diaminopropionic monohydrobromide, no serine was obtained, but *iso*serine was isolated in a 20 per cent. yield and was identified by the formation of its copper and its phenylcarbimide derivatives (compare E. Fischer and Leuchs, Abstr., 1903, i, 12). The essential action is accordingly represented by the equation :

$$NH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,HBr + AgNO_2 = NH_2\cdot CH_2\cdot CH(OH)\cdot CO_2H + AgBr + N_2 + H_2O.$$

When the mother liquor from the preparation of the *iso*serine was made alkaline and shaken with an ethereal solution of naphthalene-β-sulphonic chloride, naphthalene-β-sulphoserine was not obtained (compare E. Fischer and Bergell, Abstr., 1903, i, 24). A. McK.

Ethyl α-*iso*Nitroso-β-nitrosoaminobutyrate and its Derivatives. Hans Euler and Astrid Euler (*Ber.*, 1904, **37**, 47—49. Compare this vol., i, 146).—The compound $C_6H_9O_4N$, previously described, is shown to be identical with V. Meyer's ethyl *iso*nitrosoacetoacetate, and the original product of the action of amyl nitrite on ethyl β-aminocrotonate is therefore ethyl α-*iso*nitroso-β-nitrosoaminobutyrate, $ON\cdot N{:}CMe\cdot C({:}NO\cdot NH_4)\cdot CO_2Et$. Its conversion into an *iso*triazole is represented by the formulæ

$$NO\!\!<\!\!\begin{array}{l}N\!=\!\!=\!\!=\!CMe\\ N(OH){:}C\cdot CO_2Et\end{array} \longrightarrow HO\cdot N\!\!<\!\!\begin{array}{l}N\!=\!\!=\!\!=\!CMe\\ N(OH)\cdot CH\cdot CO_2Et\end{array} \longrightarrow HO\cdot N\!\!<\!\!\begin{array}{l}N{:}CMe\\ N{:}C\cdot CO_2H\end{array}.$$

T. M. L

New Bases derived from Sugars. E. Roux (*Ann. Chim. Phys.*, 1904, [viii], 1, 72—144).—An account of work already published (compare Abstr., 1901, i, 372 ; 1902, i, 266, 694 ; 1903, i, 73).

Acetylacetoneglucamine, $CH_2Ac\cdot CMe{:}N\cdot C_6H_{13}O_5$, crystallises in thin, felted needles, melts at 172°, is very soluble in water and less so in alcohol ; 80 per cent. alcohol dissolves about 6 per cent. on boiling and only 1·6 per cent. at the ordinary temperature. M. A. W.

Action of Ammonia on Itaconic Anhydride. Jone Foà (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1903, [iii], 9, 112—117).—The action of ammonia in alcoholic or benzene solution on itaconic anhydride

at the ordinary temperature or at 109° gives, after several hours, *itaconamide*, $CO_2H\cdot C_3H_4\cdot CO\cdot NH_2$, as sole product; it crystallises from alcohol in colourless needles and melts at 147—148°. At 180°, the *diamide*, $CH_2\colon C(CO\cdot NH_2)\cdot CH_2\cdot CO\cdot NH_2$, is formed. It thus appears that the double linking in itaconic anhydride is different in its nature to that of maleic and citraconic anhydrides, which at once interact additively with ammonia forming amino-acids. W. A. D.

Action of Methylamine on Citraconic Anhydride. SALVATORE GULLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1903, [iii], 9, 164—167).—On adding a solution of methylamine in benzene to citraconic anhydride dissolved in the same solvent, a *citraconmethylamic acid*,

$$CO_2H\cdot CH\colon CMe\cdot CO\cdot NHMe \text{ or } CO_2H\cdot CMe\colon CH\cdot CO\cdot NHMe,$$

is obtained; it crystallises from absolute alcohol in white, deliquescent needles with a sweet taste, melts at 114—116°, and gives a *dibromide*, $C_6H_9O_3NBr_2$, also crystallising in small, deliquescent needles. From the benzene mother liquors of the acid, *methylamine citraconate*, $CO_2H\cdot C_3H_4\cdot CO\cdot ONH_3Me$, is obtained in silky needles melting at 120—122°.

Methylaminomethylaspartic acid is probably formed when molecular quantities of methylamine and citraconic anhydride are heated together in alcoholic solution at 105—110°, but cannot be isolated from the syrupy product. W. A. D.

Action of Hydroxylamine on Unsaturated Esters. CARL D. HARRIES and WILHELM HAARMANN (*Ber.*, 1904, 37, 252—261. Compare Posner, this vol., i, 160).—*Methyl hydroxylaminodiacrylate-hydroxamic acid*, $OH\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot N(OH)\cdot CH_2\cdot CH_2\cdot CO_2Me$, prepared by the interaction of methyl acrylate and hydroxylamine in presence of sodium, crystallises in nacreous, glistening needles melting at 124°, decomposes on keeping, gives a red coloration with ferric chloride, and reduces Fehling's solution in the cold.

The *oxalate* of *methyl hydroxylaminodiacrylate*,

$$HO\cdot N(CH_2\cdot CH_2\cdot CO_2Me)_2,C_2O_4H_2,$$

is obtained by leaving the mother liquors from the above reaction in contact with anhydrous oxalic acid; it sinters at 125° and melts at 131—132°. The *hydrochloride* crystallises in plates, which sinter at 82° and melt at 92°.

[With ARTHUR STÄHLER.]—*Methylsantolate*, $C_{15}H_{21}OMe$, can be prepared either by direct esterification of santolic acid with methyl alcohol and sulphuric acid, or, better, by reducing methyl santonate with sodium amalgam. It crystallises in long, colourless needles melting at 111—114°, and forms an *acetate* which crystallises from alcohol in white plates melting at 151°. E. F. A.

Compounds of Bismuth Salts with Thiocarbamide. KARL A. HOFMANN and K. L. GONDER (*Ber.*, 1904, 37, 242—245).—Bismuth nitrate and thiocarbamide react in cold alcoholic solution forming a compound, $Bi(CSN_2H_4)_3(NO_3)_2\cdot OH$, crystallising in citron-yellow plates; at 70°, red, prismatic needles belonging to the triclinic system are formed, having the formula $Bi(CSN_2H_4)_3(NO_3)_2\cdot CSN_2H_3$. Inter-

action in aqueous solution at 80° gives rise to a basic nitrate, $Bi(CSN_2H_4)_5(NO_3)_2 \cdot OH$. Bismuth chloride and thiocarbamide interact in alcoholic solution giving rise to a compound $Bi(CSN_2H_4)_2Cl_3$, crystallising in yellow rosettes, whereas in aqueous solution a red, crystalline substance, $Bi(CSN_2H_4)_3Cl_3$, is formed. As all these compounds are well characterised, it is hoped to use them for the separation of bismuth from polonium. E. F. A.

The Amphoteric Character of Cacodylic Acid. JAN VON ZAWIDZKI (*Ber.*, 1904, **37**, 153—154).—The author's former paper (Abstr., 1903, i, 801) contained an error in calculation. The dissociation constant for cacodylic acid as a base at 0° should be $4 \cdot 15 \times 10^{-14}$, therefore ten times smaller than at 25°. The agreement of the values of K_B at 0° and 25° may be accidental, owing to the impurity of the water used, and both constants may have a considerable temperature-coefficient.

Both pseudo-acids and pseudo-bases are to be regarded as special cases of amphoteric electrolytes. C. H. D.

Preparation of Alkyl and Aryl Tin Compounds. PAUL PFEIFFER and K. SCHNURMANN (*Ber.*, 1904, **37**, 319—322).—Tin tetraethyl, $SnEt_4$, prepared by the action of magnesium ethyl bromide on tin tetrabromide, boils at 175° and is obtained free from triethylstannic bromide; the yield was 70 per cent. of the theoretical quantity, and 73 per cent. when stannic chloride was used. If only the theoretical quantity of ethyl bromide is used, triethylstannic bromide is produced, which, when extracted with ether and dried with potassium carbonate, is converted into a *triethylstannic carbonate*, $(SnEt_3)_2CO_3$, which, after distillation, separates in clear, transparent crystals and melts at 120°. The same method gave a yield of 81 per cent. of crude tin tetraphenyl and a yield of 57 per cent. of the pure product melting at 220° (Polis gives 225°).

Tribenzylstannic chloride, $Sn(CH_2Ph)_3Cl$, forms glistening, white needles, melts at 127—130°, and decomposes when distilled.

T. M. L.

Fluorobenzene and some of its Derivatives. ARNOLD F. HOLLEMAN and J. W. BEEKMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, **6**, 327—331. Compare Abstr., 1902, i, 87).—Aniline sulphate was diazotised and the ice-cold solution poured with vigorous stirring into 55 per cent. hydrofluoric acid, heated nearly to the boiling point in a copper vessel. The fluorobenzene which distilled over was condensed by a freezing mixture.

p- and *m*-Fluoronitrobenzenes were prepared in an analogous manner from the corresponding nitroanilines. The three fluorotoluenes were also prepared from the toluidines. Anthranilic acid gave a small yield of *o*-fluorobenzoic acid, the main product being salicylic acid.

m-*Fluoronitrobenzene* melts at 1·7°, boils at 205°, and has the sp. gr. 1·2532 at 84·48°. p-*Fluoronitrobenzene* melts at 26·5°, boils at 205°, and has the sp. gr. 1·2583 at 84·48°. p-*Fluoroaniline* boils at

187°. 4-*Fluoro*-1-*nitro*-2-*aminobenzene* melts at 98°. Fluorobenzene melts at 41·2°, boils at 85°, and has the sp. gr. 1·0236 at 20°/4°.

Very little diphenyl was obtained by the action of sodium on an ethereal solution of fluorobenzene. Sodium does not abstract fluorine from an alcoholic solution of fluorobenzene. *m*- and *p*-Fluoronitrobenzenes, when heated with sodium methoxide, are quantitatively converted into the corresponding nitroanisoles. A. McK.

Oxidation of *o*-Nitrotoluene Charles Lauth (*Bull. Soc. chim.*, 1904, [iii], 31, 133—134).—When *o*-nitrotoluene is oxidised with chromic acid mixture at 10—15°, only 6 to 8 per cent. of *o*-nitrobenzaldehyde is obtained. By suitably modifying the conditions, a yield of 80 per cent. of *o*-nitrobenzoic acid is procured, but no practical method of converting the acid into the aldehyde was found. With nitric acid, there was either no action or *o*-nitrobenzoic acid was produced, accompanied in some cases by nitrocresol. When potassium nitrate was added to a solution of *o*-nitrotoluene in sulphuric acid, there was formed, at 100°, 1 : 2 : 4-trinitrotoluene. When the substance was warmed with nitric acid in presence of reducing agents, small quantities of the aldehyde were obtained. "Nitrous fumes," prepared by the action of nitric acid on arsenious oxide, when passed into *o*-nitrotoluene at 150—200° gave *o*-nitrobenzaldehyde at first and the corresponding acid eventually. Nitrogen peroxide, prepared by heating lead nitrate, transformed *o*-nitrotoluene completely into *o*-nitrobenzoic acid. T. A. H.

Additive Reactions of Sulphinic Acids. Elmer P. Kohler and Marie Reimer (*Amer. Chem. J.*, 1904, 31, 163—184).—Sulphinic acids readily unite with aliphatic aldehydes with formation of hydroxysulphones. These compounds are unstable ; they gradually undergo decomposition in the air, and in solution are rapidly dissociated into their components. The following compounds were obtained by the action of toluene-*p*-sulphinic acid on acetaldehyde, *iso*butyraldehyde, and heptaldehyde respectively. p-*Tolylsulphone-ethyl alcohol*,

$$C_7H_7·SO_2·CHMe·OH,$$

crystallises in thick plates, softens at 52°, and is completely melted at 72°. p-*Tolylsulphoneisobutyl alcohol*, $C_7H_7·SO_2·CH(OH)·CHMe_2$, crystallises from ether in colourless needles. p-*Tolylsulphoneheptyl alcohol*, $C_7H_7·SO_2·CH(OH)·C_6H_{13}$, crystallises in white, slender needles and is decomposed on heating.

Toluene-*p*-sulphinic acid yields a similar series of compounds with aromatic aldehydes, but these substances are much more stable than those obtained with the aliphatic aldehydes. The two following compounds were obtained with *m*- and *p*-nitrobenzaldehyde respectively. p-*Tolylsulphone*-m-*nitrophenylcarbinol*,

$$C_7H_7·SO_2·CH(OH)·C_6H_4·NO_2,$$

crystallises in white, slender needles and melts at 110°. p-*Tolylsulphone*-p-*nitrophenylcarbinol* crystallises in pale yellow needles and melts at 116° ; it is decomposed by aniline, and it dissolves in acetic anhydride with formation of the acetal of *p*-nitrobenzaldehyde.

Toluene-*p*-sulphinic acid combines with cinnamaldehyde with

formation of a monosulphone and a disulphone. The *monosulphone*, $C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot CHO$, forms white, globular masses of crystals and melts at 78°; it unites with potassium hydrogen sulphite to form a crystalline compound, and when oxidised with dilute nitric acid it yields β-*p*-tolylsulphone-β-phenylpropionic acid. The *disulphone*,

$$C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot CH(OH)\cdot SO_2\cdot C_7H_7,$$

crystallises in white needles and melts and decomposes at about 126°.

β-p-*Tolylsulphone-β-phenylpropionic acid*,

$$C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot CO_2H,$$

prepared by the action of toluene-*p*-sulphinic acid on cinnamic acid, crystallises from hot water in slender needles, melts at 197—198°, and is readily soluble in alcohol or ether; its *methyl* ester melts at 156°; its *sodium*, *calcium*, and *barium* salts are described.

β-*Phenylsulphone-β-phenylpropionic acid*, $SO_2Ph\cdot CHPh\cdot CH_2\cdot CO_2H$, obtained by the action of benzenesulphinic acid on cinnamic acid, crystallises from hot water in lustrous plates, melts at 173°, and is readily soluble in alcohol or ether; its *ethyl* ester melts at 139°; the *barium* salt is described.

β-p-*Tolylsulphonepropionic acid*, $C_7H_7\cdot SO_2\cdot CH_2\cdot CH_2\cdot CO_2H$, is formed by the action of toluene-*p*-sulphinic acid on fumaric or maleic acid, but is best obtained in a pure state by treating β-iodopropionic acid with sodium *p*-toluenesulphinate; it crystallises in needles and melts at 110—113°.

p-*Tolylsulphonepyrotartaric acid*, $C_7H_7\cdot SO_2\cdot CMe(CO_2H)\cdot CH_2\cdot CO_2H$, obtained by the action of toluene-*p*-sulphinic acid on citraconic acid, crystallises in small, lustrous prisms, melts at 169—171°, and is extremely soluble in alcohol, ether, or acetone; its *sodium* salt is described.

Toluene-*p*-sulphinic acid readily unites with unsaturated ketones. The following compounds were obtained by its combination with benzylideneacetone, dibenzylideneacetone, benzylideneacetophenone, cinnamylideneacetone, and cinnamylideneacetophenone respectively. The *compound*, $C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot COMe$, crystallises from alcohol in white, slender needles and is decomposed by bleaching powder with formation of chloroform and β-*p*-tolylsulphone-β-phenylpropionic acid; when treated with phenylhydrazine, it yields the phenylhydrazone of benzylideneacetone, phenylhydrazine toluene-*p*-sulphinate, and 1:5-*diphenyl-3-methylpyrazoline*, $NPh{<}{\genfrac{}{}{0pt}{}{-CHPh}{N:CMe}}{>}CH_2$, which forms long, pale yellow crystals and melts at 114°. The *compound*,

$$C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot CO\cdot CH\colon CHPh,$$

crystallises in long, slender needles and melts at 189°; on oxidation with potassium permanganate, it is converted into benzaldehyde, benzoic acid, and β-*p*-tolylsulphone-β-phenylpropionic acid. It unites with 2 atoms of bromine to form a *dibromo*-compound which crystallises in needles. The *compound*, $C_{22}H_{20}O_3S$, formed by the action of toluene-*p*-sulphinic acid on benzylideneacetophenone, crystallises in needles and melts at 169—170°. The *compound*,

$$C_7H_7\cdot SO_2\cdot CH(CH_2\cdot COMe)\cdot CH\colon CHPh,$$

crystallises from alcohol and melts at 125—126°; when warmed with a concentrated solution of bleaching powder, it yields benzoic acid and

other products, which, on oxidation with potassium permanganate, furnish *β-p*-tolylsulphonepropionic acid. The *compound*,

$$C_7H_7 \cdot SO_2 \cdot CH(CH_2 \cdot COPh) \cdot CH:CHPh,$$

crystallises from acetone in needles and melts at 145°. E. G.

Aromatic Betaines. II. RICHARD WILLSTÄTTER and WALTER KAHN (*Ber.*, 1904, 37, 401—417. Compare Abstr., 1902, i, 266).—Unlike the fatty α-betaines, the transformation of aromatic betaines by heat is not affected by the relative position of the carbonyl and the basic group.

In the methylation of anthranilic acid by means of methyl iodide and sodium hydroxide, not more than two methyl groups can be introduced, the compound described by Lauth (Abstr., 1894, i, 86) as the hydriodide of *o*-benzobetaine being, in fact, the salt of dimethylanthranilic acid, and Lauth's dimethylanthranilic acid being methylanthranilic acid. The betaine is best prepared by methylation of methyl methylanthranilate, which is readily obtained from anthranilic acid and methyl sulphate (F. Ullmann, Abstr., 1903, i, 394). Methyl iodide converts it in the cold into *methyl dimethylanthranilate*,

$$C_6H_4(NMe)_2 \cdot CO_2Me,$$

an uncrystallisable oil boiling at 160—161° under 38 mm. or at 130—131° under 11·5 mm. pressure. The *hydriodide* forms sparingly soluble needles and leaflets and melts at 163°. Prolonged boiling with water hydrolyses the ester, forming *dimethylanthranilic acid*, crystallising from ether in long, white needles and melting at 70°, dissolving readily in water or alcohol, sparingly in cold ether. The *aurichloride*, $(C_9H_{11}O_2N)_2,HAuCl_4$, crystallises from boiling alcohol in large, yellow prisms and decomposes above 100°. *Methyl dimethylanthranilate methiodide* crystallises from water in colourless prisms and melts at 153°.

Methyl m-*dimethylaminobenzoate methiodide* forms small needles, which dissolve sparingly in alcohol or cold water and melt and decompose at 220—221°. The corresponding para-*compound* crystallises from alcohol in silvery, glistening, six-sided tablets and melts and decomposes at 170°.

o-*Benzobetaine*, $C_6H_4 < \begin{matrix} NMe_3 \\ CO \end{matrix} > O$, prepared by the action of moist silver oxide on the iodide, crystallises from absolute alcohol in highly refractive tablets and hollow pyramids, containing $\frac{1}{2}H_2O$, and melts at 224°. After removal of the water, which is only complete after heating at 120° for 2 weeks under reduced pressure, it melts at 227°. It dissolves readily in water, sparingly in cold alcohol or acetone, and is insoluble in ether. The *platinichloride* forms large tablets, the *picrate* forms slender needles. The *aurichloride* forms slender, yellow needles, darkens on heating, and melts and decomposes at 206°; the *hydriodide* forms thick, square prisms containing H_2O, and melts at 138°. Anhydrous *o*-benzobetaine is converted by heating at 240—245° into methyl dimethylanthranilate, a small quantity of dimethylaniline being always formed at the same time, and predominating when moisture is present. The latter base is removed in the form of phenyltrimethylammonium iodide by the addition of methyl iodide.

p-Benzobetaine (compare Michael and Wing, Abstr., 1886, 148) is readily prepared from *p*-aminobenzoic acid. Heating at 110° converts it quantitatively into methyl *p*-dimethylaminobenzoate.

Phenyldimethylbetaine (phenyldimethylglycine) is best prepared by the method of Reitzenstein (Abstr., 1903, i, 435), and crystallises from alcohol in aggregates of small, transparent crystals containing H_2O, and melts at 123—124°. The water is not completely removed by heating. The *picrate* forms slender needles, and decomposes at 195°. Heating the betaine at 170—175° converts it into phenyldimethylglycine, forming a *methiodide* melting at 98—99°. A small quantity of dimethylaniline is also produced. C. H. D.

Action of Nitrous Acid on Phenylcarbamide. R. DOHT and J. HAAGER (*Monatsh.*, 1903, 24, 844—856).—Phenylcarbamide reacts readily with nitrous acid with little evolution of gas. When only $1\frac{1}{2}$ mols. of hydrogen chloride are present, nitrosophenylcarbamide, $NO{\cdot}NPh{\cdot}CO{\cdot}NH_2$, is formed. In presence of an excess of hydrochloric acid, this is decomposed into diazobenzene chloride and carbamic acid, which then breaks up into water and *iso*cyanic acid. The diazobenzene chloride and *iso*cyanic acid then combine to form phenylcarbimide, nitrogen being set free. Alcoholic potassium hydroxide or potassium ethoxide reacts with nitrosophenylcarbamide, forming potassium *iso*cyanate and potassium phenylnitrosoamine. Thus, when nitrous acid reacts with phenylcarbamide, suspended in an excess of hydrochloric acid, oily drops of phenylcarbimide separate, and diazobenzene chloride is found in the solution. C. H. D.

Action of Phenylcarbimide on Certain Monohydric Alcohols. II. ARMAND BLOCH (*Bull. Soc. chim.*, 1904, [iii], 31, 71—76. Compare this vol., ii, 152).—*Cholesteryl phenylurethane*,

$$C_{26}H_{43}{\cdot}O{\cdot}CO{\cdot}NHPh,$$

obtained by heating cholesterol with phenylcarbimide at 180°, melts at 168—169°, is readily soluble in ether, chloroform, or benzene in the cold, and in alcohol or light petroleum when heated. It has $[\alpha]_D$ −28·19° at 19° in benzene when $c = 2{\cdot}07$ per cent., gives an orange-yellow coloration with sulphuric acid, and the usual cholesterol reactions with Hesse's and Salkowski's reagents. It decomposes at 68—70° when heated in test-tubes, and at 280° when heated in open vessels, evolving carbon dioxide and leaving a brown, fluorescent liquid from which aniline, diphenylcarbamide, and a crystalline *substance* melting at 138—140° were isolated.

When heated in a closed tube at 350°, cholesteryl phenylurethane decomposes into aniline, cholesterol, and a *cholesterilene*, $C_{26}H_{42}$, which crystallises in needles, melts at 75·5°, has $[\alpha]_D$ −97·85—98° in benzene when $c = 2{\cdot}08$ per cent., and −100·25° when $c = 1{\cdot}04$ per cent., gives a citron-yellow coloration with sulphuric acid, and the usual cholesterol colour reactions.

This cholesterilene is similar to, but probably not identical with, that described by Mauthner and Suida (Abstr., 1896, i, 425), which, the author finds, melts at 74° and has $[\alpha]_D$ −71·88° at 18° in benzene when $c = 0{\cdot}626$ per cent.

Cholesteryl phenylurethane, when heated with ammonia in closed tubes, furnishes ammonium carbonate, aniline, and cholesterol; the latter has $[\alpha]_D$ $-40{\cdot}46°$ at 19° in chloroform when $c = 1{\cdot}85$ per cent., whereas commercial cholesterol, twice recrystallised from alcohol, has $[\alpha]_D$ $-40{\cdot}37°$ at 19° in chloroform when $c = 1{\cdot}80$ per cent.

When heated with aniline, either in closed tubes or under atmospheric pressure, cholesteryl phenylurethane decomposes partially into diphenylcarbamide and cholesterol; it is scarcely attacked by barium hydroxide or a 10 per cent. solution of potassium hydroxide, but a 50 per cent. solution of the latter decomposes it, forming carbon dioxide, aniline, and cholesterol. It is pointed out that phenylurethanes are only readily obtained from the monohydric alcohols containing less than thirty carbon atoms in the molecule, and that they are all crystalline with the exception of octyl phenylurethane.

Hexadecyl and cholesteryl phenylurethanes are exceptionally stable towards heat. T. A. H.

Condensation of Oximes with Thiocarbimides. Bronislas Pawlewski (*Ber.*, 1904, **37**, 158—160).—The thiocarbimides readily condense with oximes to form derivatives of thiocarbamide. Phenylthiocarbimide combines with α- or β-benzaldoxime, dissolved in toluene, forming diphenylthiocarbamide, $CS(NHPh)_2$. *o*-Tolylthiocarbimide and benzaldoxime form *phenyl*-o-*tolylthiocarbamide*, $C_6H_4Me{\cdot}NH{\cdot}CS{\cdot}NHPh$, crystallising from alcohol in slender, glistening needles melting at 166—168°. This does not appear to be identical with the compound obtained by Staats (Abstr., 1880, 386) from aniline and *o*-tolylthiocarbimide. *Phenyl*-p-*tolylthiocarbamide* crystallises in thick needles melting at 176—178° and is probably isomeric with the compound obtained by Staats, Gebhardt (Abstr., 1884, 1320) and Marckwald (Abstr., 1892, 1326). Camphoroxime combines slowly with phenylthiocarbimide, dissolved in benzene, and after several months *phenylcamphanylthiocarbamide*, $C_{10}H_{17}{\cdot}NH{\cdot}CS{\cdot}NHPh$, separates, crystallising from alcohol in needles and leaflets melting at 150—152°. The reaction occurs rapidly on heating. A probably isomeric compound has been obtained by Goldschmidt and Schulhof (Abstr., 1886, 557).

C. H. D.

Methyl and Ethyl Ethers of *p*-Hydroxyphenylhydroxylamine and the Derived Azoxy-compounds. Adolf Rising (*Ber.*, 1904, **37**, 43—47).—*p-Anisylhydroxylamine*, $OMe{\cdot}C_6H_4{\cdot}NH{\cdot}OH$, forms glistening, white scales or flat needles, melts at about 98°, but sometimes resolidifies at this temperature, and liberates gas when again fused to a clear liquid. *p*-Nitrosoanisole, $OMe{\cdot}C_6H_4{\cdot}NO$, crystallises from light petroleum and melts at 23°; the product melting at 32—34°, described by Baeyer and Knorr as an oxidation product from *p*-anisidine and Caro's acid, contained considerable quantities of *p*-nitroanisole. A theoretical yield of *p*-azoxyanisole was obtained by the interaction of the two preceding compounds, and the substance showed the turbidity ('liquid crystals') first described by Gattermann.

p-*Phenetylhydroxylamine*, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}OH$, forms white, glistening scales and melts at 91·5—92° when heated from 75°, but the melting

point is dependent on the rate of heating; the substance begins to decompose in the course of a few hours, but can be purified by recrystallising from ether. *p-Nitrosophenetole* crystallises from light petroleum in large, bluish-green prisms and melts at 33—34°. The *p*-azoxyphenetole prepared from these two compounds melted at 137·4—137·9° and became clear at 168—168·5°, that is, 3° above the temperatures given by Gattermann. *p*-Anisoleazoxy-*p*-phenetole, however, prepared from *p*-phenetylhydroxylamine and *p*-nitrosoanisole, melted at 93·5—94° and became clear at 149·6°, temperatures considerably higher than those recorded by Gattermann and Ritschke (Abstr., 1890, 1119). T. M. L.

Behaviour of Aminophenols towards Caro's Reagent. EUGEN BAMBERGER and MAX CZERKIS (*J. pr. Chem.*, 1903, [ii], 68, 473—480. Compare Abstr., 1903, i, 624).—Caro's reagent oxidises *o*-aminophenol to *o*-nitrophenol, together with an unknown nitroso-compound and a compound which crystallises in red needles and melts at 156·5°, and yields *o*-aminophenol on reduction. *m*-Aminophenol yields *m*-nitrophenol, 3- and 4-nitrocatechol, and *m*-azoxyphenol, $ON_2(C_6H_4{\cdot}OH)_2$ (Nölting and Federmann, *Chem. Zeit.*, 1902, 26, 52). The latter compound was also prepared from *m*-nitrophenetole by reduction to m-*ethoxyphenylhydroxylamine*, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}OH$, white, silky needles melting at 61—61·5°, and oxidation, followed by hydrolysis of the ethoxy-groups. The oxidation product from *m*-aminophenol also contains acetaldehyde, the formation of which is unexplained.

p-Aminophenol is oxidised in ethereal solution to *p*-nitrosophenol and *p*-nitrophenol; in aqueous solution, quinone and quinol are formed. C. H. D.

Oxidation of *m*- and *p*-Nitrophenols with Caro's Reagent. EUGEN BAMBERGER and MAX CZERKIS (*J. pr. Chem.*, 1903, [ii], 68, 480—485).—Caro's reagent oxidises a solution of *m*-nitrophenol in water on warming, with formation of 3- and 4-nitrocatechols, a hydroxyl group being thus directly introduced. A part of the nitrophenol is broken down, carbon dioxide being evolved, and an oily compound, showing the reactions of an organic peroxide, is formed. On distilling the oil, or on warming its aqueous solution, succinic acid is formed.

p-Nitrophenol is best oxidised by Caro's reagent in the pasty form. 4-Nitrocatechol and the oily peroxide are obtained. *o*-Nitrophenol resists oxidation; 3-nitrocatechol was isolated from the product. C. H. D.

Oxidation of Phenol with Caro's Reagent. EUGEN BAMBERGER and MAX CZERKIS (*J. pr. Chem.*, 1903, [ii], 68, 486).—Caro's reagent oxidises phenol at the ordinary temperature, forming catechol, quinhydrone, and small quantities of other compounds, not yet investigated. C. H. D.

Pyrogallol. ALFRED EINHORN, J. COBLINER, and H. PFEIFFER (*Ber.*, 1904, 37, 100—123).—It has been shown (Einhorn, Abstr., 1898, i, 409) that monohydric phenols form only carbonates of the

formula $CO(OR)_2$, whilst *o*-dihydric phenols form internal carbonates, $R''<^{O}_{O}>CO$, and *m*- and *p*-dihydric phenols form polymolecular carbonates. Pyrogallol is found to form only two carbonates, the reactions of which have now been studied.

On passing a current of phosgene gas into a solution of pyrogallol in a mixture of pyridine and xylene and boiling, an oil separates, becoming syrupy on cooling. The xylene is separated, and the oil decomposed by cooled dilute hydrochloric acid, which precipitates *pyrogallol carbonate*, $OH\cdot C_6H_3<^{O}_{O}>CO$, crystallising from benzene in colourless needles or tablets melting at 132—133°. The same product is obtained by heating pyrogallol with phenol carbonate. It has a sweet taste and dissolves sparingly in water, the solution gradually decomposing, readily soluble in ether, acetone, ethyl acetate, or acetic acid. Ferric chloride gives a violet-brown coloration, destroyed by hydrochloric acid. The molecular weight in benzene solution is normal.

Dipyrogallol tricarbonate, $CO\left(O\cdot C_6H_3<^{O}_{O}>CO\right)_2$, prepared by the same method, but employing a larger quantity of phosgene, crystallises in colourless leaflets melting at 177°, and dissolves sparingly in alcohol, ether, or benzene. It is only slowly attacked by boiling water, and even warm sodium carbonate only causes decomposition after a long time.

Benzoylpyrogallol carbonate, $OBz\cdot C_6H_3<^{O}_{O}>CO$, crystallises from benzene in white, nodular masses and melts at 149°. Ferric chloride produces no coloration.

Pyrogallol carbonate is converted by boiling with methyl alcohol into *pyrogallol methyl carbonate*, $C_6H_3(OH)_2\cdot O\cdot CO_2Me$, crystallising from a mixture of benzene and chloroform and melting at 120°. This and the similar derivatives obtained by the action of alcohols or bases on the carbonate give the green catechol coloration with ferric chloride, indicating that the two remaining hydroxyl groups are in the ortho-position. *Pyrogallol ethyl carbonate* crystallises from a mixture of chloroform and light petroleum in small, white needles and melts at 74°. *Pyrogallol diethylcarbamate*, $C_6H_3(OH)_2\cdot O\cdot CO\cdot NEt_2$, from pyrogallol carbonate and diethylamine, crystallises from alcohol in rhombic tablets and melts at 149°. Piperidine forms *pyrogallol piperidine-1-carboxylate*, $C_6H_3(OH)_2\cdot O\cdot CO\cdot C_5H_{10}N$, which crystallises from ethyl acetate in colourless needles and melts at 161°. *Pyrogallol phenylcarbamate*, $C_6H_3(OH)_2\cdot O\cdot CO\cdot NHPh$, crystallises from benzene in long needles and melts at 141°. *Pyrogallol* p-*phenetylcarbamate*, $C_6H_3(OH)_2\cdot O\cdot CO\cdot NH\cdot C_6H_4\cdot OEt$, separates from a mixture of benzene and ethyl acetate in needles melting at 162°.

Pyrogallol carbonate combines with quinoline to form a *compound*, $CO<^{O}_{O}>C_6H_3\cdot O\cdot C_9H_8N$, separating from a mixture of benzene and light petroleum in colourless needles and melting at 103°. Triethylamine forms the *compound*, $\left[CO<^{O}_{O}>C_6H_3(OH)\right]_2,NEt_3$, which may be

an oxonium compound, or may contain the second molecule of carbonate as phenol of crystallisation. It forms colourless needles, melting at 111° and decomposing on exposure to air.

Bromopyrogallol carbonate, $CO<^{O}_{O}>C_6H_2Br\cdot OH$, prepared by the action of bromine on a cooled solution of the carbonate in dry chloroform, crystallises from benzene in colourless crystals melting at 155°, dissolving readily in ether, sparingly in benzene or chloroform. The bromine atom probably occupies either the 4- or 6-position. Carbon dioxide is evolved on boiling with water, forming *bromopyrogallol*, which crystallises from benzene in thick prisms, blackens at 120°, and decomposes at about 140°. By further bromination in presence of iron, *dibromopyrogallol carbonate* is obtained in needles melting at 146°, and decomposing into *dibromopyrogallol*, which forms long needles melting at 158°, on boiling with water.

A cooled mixture of concentrated nitric and sulphuric acids converts pyrogallol carbonate into 4-(or 6-)*nitropyrogallol carbonate*,

$$CO<^{O}_{O}>C_6H_2(OH)\cdot NO_2,$$

which crystallises from chloroform in long, slightly yellow needles melting at 148—149°, and dissolves readily in ether, acetone, or ethyl acetate, sparingly in water, acetic acid, or benzene. Boiling alcohol converts it into *nitropyrogallol ethyl carbonate*,

$$NO_2\cdot C_6H_2(OH)_2\cdot O\cdot CO_2Et,$$

crystallising from dilute alcohol in yellow leaflets, melting at 134°, and dissolving in alkalis to yellow solutions. Bromine converts it into *bromonitropyrogallol ethyl carbonate*, which forms bright yellow needles melting at 172°. Boiling water decomposes nitropyrogallol carbonate, forming 4-*nitropyrogallol*, which crystallises from water or benzene in groups of needles melting at 162°, and dissolving readily in alcohol, ether, acetic acid, or ethyl acetate. The *dipotassium* and *diammonium* salts are reddish-brown, and cannot be recrystallised, the *quinoline* salt forms unstable, fluorescent, yellow needles and melts at 74°. Bromine forms *bromonitropyrogallol*, crystallising from benzene in yellow masses and melting at 122°, dissolving readily in ether, sparingly in water or chloroform. *Benzoyl*-4-*nitropyrogallol* crystallises from benzene in slender, yellow needles melting and decomposing at 214°.

Triacetyl-4-*nitropyrogallol*, $NO_2\cdot C_6H_2(OAc)_3$, forms yellow needles melting at 85°, and dissolves readily in ether, sparingly in benzene or alcohol. Nitropyrogallol may be methylated with methyl sulphate; the *trimethyl ether* separates from dilute alcohol in colourless crystals and melts at 44°. Tin and hydrochloric acid reduce nitropyrogallol to 4-*aminopyrogallol hydrochloride*, which forms colourless needles and dissolves in water and alcohol to solutions which darken when kept. Benzoyl chloride reacts with it at 150° to form 5 : 6-*dibenzoyloxy*-1-*phenylbenzoxazole*, $C_6H_2(OBz)_2<^{O}_{N}>CPh$, which crystallises from benzene-light petroleum in white needles and melts at 144°.

When a solution of aminopyrogallol hydrochloride is boiled for 8 hours, a current of carbon dioxide being passed through it, 1 : 2 : 3 : 4-*tetrahydroxybenzene* is obtained, crystallising from benzene

in colourless needles melting at 161° and dissolving readily in water ether, alcohol, or ethyl acetate. Methyl sulphate forms an ether melting at 83°, which seems to be identical with Ciamician and Silber's tetramethylapionol, melting at 89° (Abstr., 1896, i, 608). The *tetra-acetyl*-derivative crystallises from a mixture of alcohol and light petroleum in needles melting at 136°; the *tetrabenzoyl* derivative forms colourless leaflets.

Fuming nitric and sulphuric acids convert pyrogallol carbonate into 4 : 6-*dinitropyrogallol*, $C_6H(NO_2)_2(OH)_3$, which crystallises from hot water in long, yellow needles, melting at 208°, dissolving in alkalis to dark brown solutions. The *triacetyl* derivative forms colourless leaflets and melts at 154°. Reduction of the dinitro-compound with tin and hydrochloric acid gives 4 : 6-*diaminopyrogallol hydrochloride*, which reacts with benzoyl chloride to form 6-*benzoyloxy*-1 : 5-*diphenylbenzodioxazole*, $OBz\cdot C_6H\left[<^{N}_{O}>CPh\right]_2$, crystallising from benzene in colourless, felted needles and melting at 291°. Water converts the diaminohydrochloride into pentahydroxybenzene, $C_6H(OH)_5$, crystallising from benzene in microscopic needles, dissolving readily in alcohol, ether, or ethyl acetate, sparingly in water, insoluble in benzene (compare Wenzel and Weidel, this vol., i, 48). The *penta-acetyl* derivative forms colourless needles melting and decomposing at 165°.
C. H. D.

α-Phenyl-α-anisylpropene. CARL HELL and H. STOCKMAYER (*Ber.*, 1904, **37**, 225—230).—When phenyl anisyl ketone was submitted to the Grignard reaction with magnesium ethyl iodide, α-phenyl-α-anisylethylcarbinol was not isolated as a product of the action, but *α-phenyl-α-anisylpropene*, $OMe\cdot C_6H_4\cdot CPh:CHMe$, presumably formed from the carbinol by abstraction of water, was obtained instead; it separates from methyl alcohol in glistening leaflets, melts at 54°, and distils unchanged at about 312° under the ordinary pressure. When bromine is added to its chloroform solution, hydrogen bromide is evolved and *β-bromo-α-phenyl-α-anisylpropene*, $OMe\cdot C_6H_4\cdot CPh:CBrMe$, is formed; this separates from ether in tiny needles and melts at 51—52°; when bromine is added to its chloroform solution, hydrogen bromide is evolved, and a crystalline substance, $C_{16}H_{24}OBr_2$, melting at 98—99°, were isolated, the product probably being a substitution product containing bromine in the anisyl group. Bromophenylanisylpropene is not attacked by sodium ethoxide.
A. McK.

Aromatic Propene Derivatives. III. CARL HELL and H. BAUER (*Ber.*, 1904, **37**, 230—233. Compare preceding abstract).—αα-Diphenylpropene, $CPh_2:CHMe$, and α-phenyl-α-methylpropene, $CMePh:CHMe$, behave like phenylanisylpropene with respect to the action of bromine.

Diphenylethylcarbinol, $CEtPh_2\cdot OH$, prepared by the application of Grignard's reaction to benzophenone with magnesium ethyl iodide, melts at 94—95°. When boiled with acetic anhydride, it forms *αα-diphenylpropene*, which crystallises from alcohol in leaflets and melts at 52°. *β-Bromo-αα-diphenylpropene*, $CPh_2:CBrMe$, prepared by the action of bromine on a chloroform solution of diphenylpropene,

separates from alcohol in needles, melts at 48—49°, and boils at 169—170° under 12 mm. pressure. It is not attacked by sodium ethoxide. *β-Bromo-α-phenyl-α-methylpropene*, CMePh:CBrMe, prepared by the action of bromine on phenylmethylpropene (compare Klages, Abstr., 1902, i, 666; 1903, i, 19), is a yellow oil which boils at 114—116° under 13 mm. pressure. It is not attacked by sodium ethoxide. A. McK.

Preparation of Stilbene, 4-Methoxystilbene, and α-Methylstilbene. Carl Hell (*Ber.*, 1904, 37, 453—458).—Benzaldehyde is added to an ethereal solution of magnesium benzyl chloride, the mixture decomposed with water and dilute sulphuric acid, and the residue from the ethereal solution distilled. The yield of stilbene is good. If the product is not distilled, phenylbenzylcarbinol, $CH_2Ph\cdot CHPh\cdot OH$, is obtained as glistening needles melting at 66—67° (compare Limpricht and Schwanert, *Annalen*, 155, 62; Goldenberg, *ibid.*, 174, 332; Knoevenagel and Arndts, Abstr., 1902, i, 548; Sudborough, Trans., 1893, 67, 605).

Anisaldehyde and magnesium benzyl chloride yield, without distillation of the product, *p*-methoxystilbene (compare von Walther and Wetzlich, Abstr., 1900, i, 438).

Phenylbenzylmethylcarbinol, $CH_2Ph\cdot CMePh\cdot OH$, obtained from acetophenone and magnesium benzyl chloride, melts at 50—51° and distils under atmospheric pressure, or at 175° under 15 mm. pressure, without being decomposed. On treatment with acetic anhydride, it yields α-methylstilbene (compare Abstr., 1902, i, 668). J. J. S.

Reaction between Benzene and Formaldehyde. Alexander M. Nastukoff (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 824—831).—The interaction of benzene and formaldehyde in presence of concentrated sulphuric acid yields a compound to which the author gives the name *phenylformol*. It is insoluble in all solvents and differs from the compound formed from benzene and cellulose (see Abstr., 1902, i, 362 and 747) in being very stable towards the action of reagents; thus, excess of chromic acid in acetic acid solution, phosphorus pentachloride, and hydrobromic acid in a sealed tube are all without action on it. Its composition is: carbon, 87·29; hydrogen, 6·78; oxygen, 5·23; and sulphur, 0·70 per cent. On dry distillation, it yields about 50 per cent. of its weight of an oil containing 12 per cent. (on the weight of oil) of diphenylmethane, 7 of toluene, 3 of phenyl-*p*-tolylmethane, 2 of *p*-xylene, 2 of anthracene and synanthrene, and 1 of benzene. Working under definite conditions, this method may be employed for the preparation of diphenylmethane from formalin.

The formation of diphenylmethane shows that the phenyl groups replace the oxygen or the hydroxyl, whilst in the case of the cellulose compound (*loc. cit.*) they replace the hydrogen. T. H. P.

Constitution of Phenylcinnamenylacrylic Acid Dibromide. Arthur Michael and Virgil L. Leighton (*J. pr. Chem.*, 1903, [ii], 68, 521—534).—The dibromide of phenylcinnamenylacrylic acid is assumed by Thiele and Rössner (Abstr., 1899, i, 612) to contain the bromine

atoms in the $\alpha\delta$-positions, on account of its conversion by alkali into diphenylhydrofuran. The conversion into a γ-lactone by heating with diethylaniline, however, suggests the $\gamma\delta$-positions for the bromine atoms, and is explained by Thiele as being due to the formation and dissociation of diethylaniline hydrobromide. The formation of lactone takes place, however, at 150°, at which temperature the diethylaniline salt is not dissociated. The reactions are now shown to be explicable on the assumption of the $\gamma\delta$-constitution.

The addition of bromine to phenylcinnamenylacrylic acid is best carried out at 0° in carbon disulphide solution in direct sunlight. After recrystallisation from alcohol, the dibromide melts at 180—181°. An amorphous isomeride is also obtained, yielding a *methyl* ester, which crystallises from methyl alcohol in six-sided prisms and melts at 133—134°. A portion of the ester remains uncrystallisable and appears to contain a third isomeride.

Methyl phenylcinnamenylacrylate, crystallising from methyl alcohol in thick prisms and melting at 82—83°, combines with bromine to form a dibromide identical with that obtained by Thiele by esterifying the dibromide of the acid, and melting at 118°. An amorphous dibromide was also obtained.

Oxidation of the acid dibromide gives a means of distinguishing between the $\alpha\delta$- and $\gamma\delta$-constitutions: $CO_2H{\cdot}CPhBr{\cdot}CH{:}CH{\cdot}CHBrPh$ giving $CPhBr{:}(CO_2H)_2$, and $CO_2H{\cdot}CHPh{:}CH{\cdot}CHBr{\cdot}CHBrPh$ giving $CHPhBr{\cdot}CHBr{\cdot}CO_2H$ and $COPh{\cdot}CO_2H$. The oxidation is carried out by means of potassium permanganate in acetone solution (F. Sachs, Abstr., 1901, i, 272), and is imperfect, but benzoylformic acid was recognised among the products. Better results are obtained from the methyl ester melting at 118°, which yields the dibromide of cinnamic acid and benzoylformic acid on careful oxidation with potassium permanganate in acetone solution. Benzoic acid is also formed by the decomposition of cinnamic acid dibromide into hydrogen bromide and α-bromocinnamic acid, the latter being then oxidised to benzoic acid. The isomeric methyl ester dibromide melting at 134° yielded methyl benzoylformate on oxidation.

A solution of potassium hydroxide (1—2 mols.) converts the acid dibromide, at the ordinary temperature, into diphenyldihydrofuran. In this case, the γ-bromine atom is probably replaced by hydroxyl, potassium bromide and carbon dioxide being removed at the same time, and the unsaturated carbinol then passes into the furan derivative, $O{<}\begin{matrix}CHPh{\cdot}CH\\ CHPh{\cdot}CH\end{matrix}$ (the two CH joined by a double bond). When a larger quantity of potassium hydroxide is employed, hydrogen bromide is rapidly removed with the formation of phenylbromocinnamenylacrylic acid. Potassium hydroxide converts the methyl ester dibromide, melting at 134°, into *methyl phenylbromo cinnamenylacrylate*, crystallising from methyl alcohol and melting at 81—82°, isomeric with the ester prepared by Thiele melting at 128°.

When the liquid acid dibromide reacts with a small quantity of potassium hydroxide, diphenyldihydrofuran is formed; excess of alkali forms *phenylcinnamenylacrylic acid*, melting at 200—201°, and isomeric with Thiele and Rössner's acid, together with a crystalline acid which was not obtained in a pure state. C. H. D.

Nitrophthalaldehydic Acids. RUDOLF WEGSCHEIDER and LEO KUŠY VON DÚBRAV (*Monatsh.*, 1903, 24, 805—831).—Phthalaldehydic acid (*o*-aldehydobenzoic acid) is not nitrated by boiling with glacial acetic acid and fuming nitric acid, anhydrides being formed. A better result is obtained when a solution of phthalaldehydic acid in cold concentrated sulphuric acid is nitrated with potassium nitrate and the product poured into water. A white precipitate separates, consisting of a mixture of the anhydrides of 3- and 5-nitrophthalaldehydic acids. The filtrate contains chiefly the 5-nitro-acid. The two acids are separated by fractional crystallisation and by conversion into the copper salts. Phthalaldehydic acid is but little acted on by sulphuric acid, even at 105°, so that the formation of anhydrides during nitration probably occurs after the introduction of the nitro-group.

5-*Nitrophthalaldehydic acid*, $CHO\cdot C_6H_3(NO_2)\cdot CO_2H$, crystallises from water in yellow leaflets and melts at 159—161°, dissolving readily in ether, alcohol, or acetic acid, sparingly in benzene. Phenylhydrazine gives with it a red precipitate. Concentrated sulphuric acid converts it into an *anhydride*, $C_{16}H_8O_9N_2$, crystallising from acetone in small, white, silky needles and melting at 224—226°. The same anhydride is also obtained, mixed with unaltered acid, when the acid is heated at 174°. Oxidation with potassium permanganate in alkaline solution forms 4-nitrophthalic acid. *p*-Nitrobenzaldehyde is obtained on heating the silver salt at 250° under 12 mm. pressure.

3-*Nitrophthalaldehydic acid*, $C_8H_8O_5N,H_2O$, crystallises from water and shows a variable melting point, but after drying at 100° and crystallising from chloroform, forms aggregates of faintly-yellow needles and melts at 156—157°. Potassium permanganate oxidises it to 3-nitrophthalic acid, and *o*-nitrobenzaldehyde is obtained on heating the silver salt. The *anhydride* melts at 244—248°, or probably higher.

5-Nitrophthalaldehydic acid combines on warming with methyl alcohol to form the ψ-*methyl* ester, $NO_2\cdot C_6H_3<\begin{matrix}CO\\CH(OMe)\end{matrix}>O$, crystallising from benzene and melting at 101—103°; it is hydrolysed when boiled with water. The true *methyl* ester, prepared by warming the silver salt with methyl iodide, crystallises from a mixture of benzene and light petroleum and melts at 85—86°. Potassium permanganate oxidises it to 2-*methyl hydrogen* 4-*nitrophthalate*, crystallising from dry benzene in yellow needles and melting at 140—142°.

3-Nitrophthalaldehydic acid behaves in a similar manner. The ψ-*methyl* ester, prepared by heating the acid with methyl alcohol at 100°, crystallises from methyl alcohol in colourless prisms and melts at 106—108°. The true *methyl* ester, prepared from the silver salt and methyl iodide or by methylating the acid with methyl alcohol and hydrogen chloride in the cold, melts at 145—146°. The true ester is in both cases more stable towards water than the ψ-ester. C. H. D.

An Alcohol derived from Coumarin and its Conversion into a Coumarone Derivative. RICHARD STOERMER and ED. OETKER (*Ber.*, 1904, 37, 192—203).—The yield of 4-chloromethylsalicylaldehyde by Behn and Stoermer's method (Abstr., 1901, i, 426) may be increased by hydrolysing the oily by-product, which consists of the ether,

$[CHO\cdot C_6H_3(OH)\cdot CH_2]_2O$, with gaseous hydrogen chloride in alcoholic ethereal solution.

6-*Acetoxymethylcoumarin*, $6OAc\cdot CH_2\cdot C_6H_3{<}\substack{O\text{---}CO \\ CH:CH}$, obtained by the action of acetic anhydride and anhydrous sodium acetate on 4-hydroxymethylsalicylaldehyde and subsequent distillation under reduced pressure, crystallises from alcohol in large, colourless plates melting at 108—109°, dissolves readily in alcohol, chloroform, or acetic acid, and boils at 205—207° under 10 mm. pressure. When boiled with concentrated hydrochloric acid, it yields 6-*chloromethylcoumarin*, $CH_2Cl\cdot C_6H_3{<}\substack{O\text{---}CO \\ CH:CH}$, which crystallises from a mixture of benzene and light petroleum in colourless needles melting at 140—141°. When boiled with water, the chloro-derivative is converted into the corresponding alcohol, *coumarincarbinol*, $OH\cdot CH_2\cdot C_6H_3{<}\substack{O\text{---}CO \\ CH:CH}$, which melts at 150°. On oxidation, the carbinol yields *coumarinaldehyde* in the form of colourless needles melting at 187°; its *oxime* melts at 223°, and its *semicarbazone* sinters at 305°, but is not melted at 320° *Coumarin*-6-*carboxylic acid*, $CO_2H\cdot C_6H_3{<}\substack{O\text{---}CO \\ CH:CH}$, obtained by oxidising the aldehyde, melts and decomposes at 267—268°, and the *methyl* ester crystallises from benzene in colourless needles melting at 174°.

A mixture of mono- and di-bromo-derivatives is obtained when the 6-acetoxymethylcoumarin is brominated in diffused daylight in carbon tetrachloride solution. This mixture, when warmed with alcoholic potash, yields 4-*ethoxymethylcoumarilic acid*,

$$OEt\cdot CH_2\cdot C_6H_3{<}\substack{-O- \\ CH}{>}C\cdot CO_2H,$$

and the *ether* of 4-*hydroxymethylcoumarilic acid*,

$$O\left(CH_2\cdot C_6H_3{<}\substack{-O- \\ CH}{>}C\cdot CO_2H\right)_2,$$

which may be separated by fractional crystallisation from water. The ethoxy-acid crystallises from a mixture of benzene and light petroleum in pliable needles melting at 163—164° and only sparingly soluble in water; the *calcium* salt crystallises in plates and is readily soluble in water. Both the ethoxy-acid and the ether of the hydroxy-acid, when warmed with alcoholic hydrogen chloride, yield *ethyl* 4-*chloromethylcoumarilate*, $C_{12}H_{11}O_3Cl$, which crystallises from benzene in monoclinic prisms melting at 65—66°. 4-*Hydroxymethylcoumarilic acid*, obtained by the action of aqueous potash on the chlorinated ester, forms a colourless, microcrystalline powder very sparingly soluble in water; the *calcium* salt is readily soluble. The hydroxy-acid, when oxidised with chromic anhydride, yields 1 : 4-*coumaronedicarboxylic acid*, $CO_2H\cdot C_6H_3{<}\substack{-O- \\ CH}{>}C\cdot CO_2H$, as a white powder which is not melted at 310°.

4-*Hydroxymethylcoumarone* (*coumaryl*-4-*carbinol*),

$$OH\cdot CH_2\cdot C_6H_3{<}\substack{-O- \\ CH}{>}CH,$$

may be obtained by distilling mercurous hydroxymethylcoumarilate under a pressure of 10—15 mm., and is best isolated as its *phenylurethane* derivative, $C_{16}H_{13}O_3N$, which melts at 90°. The alcohol melts at 26—27° and distils at 147—150° under 12 mm. pressure. An aldehyde, the semicarbazone of which melts at 232°, and an oil, probably 4-methylcoumarone, are also formed during the distillation of the mercurous salt. J. J. S.

Constitution of Coumarinic Acid. WALTHER BORSCHE (*Ber.*, 1904, 37, 346—348).—The author has studied the constitution of the two isomeric forms of hydroxycinnamic acid. Coumarinic and coumaric acids are identical in structure, and are regarded as exhibiting *cis-trans*-isomerism, thus: $\begin{matrix} OH\cdot C_6H_4\cdot CH \\ \| \\ CO_2H\cdot CH \end{matrix}$ and

$$\begin{matrix} OH\cdot C_6H_4\cdot CH \\ \| \\ HC\cdot CO_2H \end{matrix}.$$

The formula, representing coumarinic acid as a cyclic anhydride of an ortho-form of *o*-hydroxyphenylacrylic acid, is discarded.

Coumarin was converted into potassium coumarinate and then coupled with phenyldiazonium chloride. Glistening leaflets of benzene azocoumarin melting at 158° were isolated. That the substance thus obtained has the structure $PhN_2\cdot C\!<\!\begin{matrix} CH\text{——}C\cdot CH{:}CH \\ CH{:}CH\cdot C\text{—}O\text{—}CO \end{matrix}$, and not $C_6H_4\!<\!\begin{matrix} CH{:}C\cdot N_2Ph \\ O\text{—}CO \end{matrix}$, is proved by the formation of benzeneazocoumarin from benzeneazosalicylaldehyde by the Perkin reaction. A. McK.

Ether-esters of β-Resorcylic, Orsellinic, and Orcinolcarboxylic Acids. JOSEF HERZIG and FRANZ WENZEL (*Monatsh.*, 1903, 24, 881—914).—From the results obtained by Herzig and Pollak from gallic acid and pyrogallolcarboxylic acid (Abstr., 1903, i, 89, 346), β-resorcylic, orsellinic, and orcinolcarboxylic acids should readily yield monoether-esters, but should only form diether-esters with difficulty in presence of a large excess of diazomethane, and this is found to be the case.

[With BERNHARD BATSCHA.]—*Methyl 2-hydroxy-4-methoxybenzoate*, $OH\cdot C_6H_3(OMe)\cdot CO_2Me$, from β-resorcylic acid and diazomethane, melts at 48—50°, gives an intense reddish-violet coloration with ferric chloride, and dissolves in dilute potassium hydroxide. Methyl iodide forms *methyl 2 : 4-dimethoxybenzoate*, which is an oil. The ethyl ether-ester melts at 53—54° (compare Perkin, Trans., 1895, 67, 990, and Gregor, Abstr., 1896, i, 171), and dissolves in potassium hydroxide, although less readily than the methyl ether. Ethyl iodide and potassium hydroxide form the *diethyl ether-ester*, which is also oily and yields 2 : 4-diethoxybenzoic acid on hydrolysis.

[With P. KURZWEIL.]—*Methyl orcinolcarboxylate* (*methyl 4 : 6-dihydroxy-2-methylbenzoate*), $C_6H_2Me(OH)_2\cdot CO_2Me$, from orcinolcarboxylic acid and diazomethane, crystallises from alcohol in long, colourless needles and melts at 98—99°. The further action of diazomethane

forms the *methoxy*-derivative, melting at 95—97° and dissolving in potassium hydroxide, and the *dimethoxy*-derivative,

$$C_6H_2Me(OMe)_2 \cdot CO_2Me,$$

short prisms melting at 80—84°, insoluble in potassium hydroxide. On hydrolysis, the two ethers yield the *ether-acid*, decomposing at 169—170°, and the *diether-acid*, decomposing at 178°, respectively.

Methyl orsellinate (methyl 2 : 6-dihydroxy-4-methylbenzoate) reacts with diazomethane, forming the *methoxy*-derivative,

$$OH \cdot C_6H_2Me(OMe) \cdot CO_2Me,$$

which crystallises in narrow, white leaflets melting at 63—65°, and the *dimethoxy*-derivative, which was not isolated in a pure state. The *ether-acid* and *diether-acid* melt at 145—146° and 140° respectively.

The oxidation of orcinol to orcein by hydrogen peroxide and ammonia, observed by Zulkowsky and Peters (Abstr., 1890, 1405), does not occur in the case of orcinolcarboxylic acid or its ester, or of the ethers or ester of orsellinic acid. Orsellinic acid, however, yields a violet dye, probably identical with orcein.

[With F. HAISER.]—Methylresorcinol (2 : 6-dihydroxytoluene) is readily prepared by methylating β-resorcylic acid with sodium and methyl iodide, and acting with hydriodic acid on the resulting 2-methoxy-6-hydroxytoluene-4-carboxylic acid, carbon dioxide being removed; it melts at 116—121° and boils at 264° (uncorr.) (compare Ullmann, Abstr., 1884, 1317). The *benzoyl* derivative crystallises from dilute alcohol and melts at 101—103°. The anhydrous sodium salt reacts with carbon dioxide at 180° under 6 atmospheres pressure, forming methylresorcylic acid, the methyl ester of which melts at 130—132°, but is evidently identical with the ester described by Batscha (Abstr., 1903, i, 491).

[With P. KURZWEIL.]—Methyl iodide and sodium convert orcinolcarboxylic acid into a mixture consisting of a compound soluble in potassium hydroxide, which was not further investigated, and an insoluble *compound* containing no methoxyl or carboxyl, which seems to be $CO<\begin{matrix}CMe_2 \cdot CMe \\ CMe_2 - CO\end{matrix}>CH$, together with two crystalline compounds, $C_{11}H_{14}O_4$, melting at 115—117°, and $C_9H_{12}O_2$, melting at 160—162°, the investigation of which is not yet completed. C. H. D.

Bismuth Phthalate and Mellitate and Pyrophoric Bismuth. PAUL THIBAULT (*Bull. Soc. chim.*, 1904, [iii], 31, 135—137. Compare Abstr., 1902, i, 290).—When anhydrous bismuth oxide is treated with excess of phthalic acid in presence of boiling water, it is transformed in the course of from 10 to 12 hours into a *bismuth phthalate* having the composition $2Bi_2(C_8H_4O_4)_3,Bi_2O_3$: this crystallises in needles, decomposes at 300°, is dissociated by water, and is insoluble in ordinary solvents, but is decomposed by mineral acids and by alkalis.

Anhydrous bismuth oxide is not acted on by either *iso*- or *meta*-phthalic acid, and the hydrated oxide is not attacked by any of the three phthalic acids.

Warm aqueous solutions of mellitic acid act rapidly on either anhydrous or hydrated bismuth oxide, producing *bismuth mellitate*,

$Bi_2C_{12}O_{12}$, which forms acicular crystals, has a sp. gr. 4·04 at 20°, is insoluble in ordinary solvents, including acetic acid, but is decomposed by mineral acids. When heated under reduced pressure in closed tubes, the salt begins to decompose about 350°, and beyond this temperature evolves carbon dioxide and is converted into a mass of carbonaceous matter containing finely-divided bismuth. This product is slowly attacked by hydrochloric acid and vigorously by nitric acid, and when thrown into the air spontaneously inflames, producing vapours of bismuth oxide. No mellitic acid sublimes during the pyrogenic decomposition of bismuth mellitate. T. A. H.

Halogen Substitution Products of α- and γ-Truxillic Acid.

RUDOLPH KRAUSS (*Ber.*, 1904, 37, 216—224. Compare Abstr., 1902, i, 785).—*Methyl dibromo-α-truxillate*, prepared by brominating methyl α-truxillate, crystallises from methyl alcohol in white needles and melts at 172°.

Ethyl hexachloro-α-truxillate, $C_{16}H_8Cl_6(CO_2Et)_2$, prepared by chlorinating ethyl α-truxillate at 50°, melts at 178°, whilst *methyl hexachloro-α-truxillate* crystallises in needles and melts at 215°.

Hexachloro-α-truxillic acid, prepared by hydrolysing the latter compound, separates from alcohol in needles and melts at 316°; its solution in sodium carbonate does not reduce permanganate. On distillation, it yields 2 : 4-*β trichlorocinnamic acid*, which forms yellow needles, melts at 173°, and reduces permanganate. That the latter acid was not an α-acid was proved by its behaviour on oxidation with potassium permanganate, since there was no evidence for the formation of dichlorobenzaldehyde when an insufficiency of the oxidising agent was used, the acid obtained being 2 : 4-*dichlorobenzoic acid*, which crystallises in needles and melts at 156—158°.

Ethyl pentachloro-α-truxillate, prepared by chlorinating ethyl-α-truxillate on a boiling water-bath, melts at 142°. *Methyl pentachloro-α-truxillate* forms needles and melts at 176°. *Pentachloro-α-truxillic acid* separates from alcohol in small needles and melts at 274°; when distilled, it forms a mixture of dichloro- and trichloro-cinnamic acids, which on oxidation yields 2 : 4-dichlorobenzoic acid.

Methyl dibromo-γ-truxillate, prepared by brominating methyl-γ-truxillate, melts at 163°. *Dibromo-γ-truxillic acid* separates from alcohol in tiny needles and melts at 280°; when distilled, it forms *p*-bromocinnamic acid. *Methyl* p-*bromocinnamate* crystallises in needles and melts at 79—80°. *p*-Bromobenzoic acid is formed by the oxidation of *p*-bromocinnamic acid by permanganate. *Methyl hexachloro-γ-truxillate* separates from alcohol in tiny needles and melts at 180—182°. *Hexachloro-γ-truxillic acid* separates from alcohol in small needles, melts at 285°, and does not reduce permanganate. When distilled, it forms 2 : 4-*β*-trichlorocinnamic acid, since the oxidation of the product yields 2 : 4-dichlorobenzoic acid.

The corresponding halogen derivatives of the stereoisomeric α- and γ-truxillic acids are accordingly very similar; the derivatives of the γ-acid have lower melting points than the corresponding derivatives of the α-acid.

The constitution of pentachloro-α-truxillic acid is

$$\begin{array}{l}(2:4)C_6H_3Cl_2\cdot \underset{|}{C}Cl\cdot \underset{|}{C}H\cdot CO_2H \\ \qquad\qquad CO_2H\cdot CH\cdot CH\cdot C_6H_3Cl_2(2':4')\end{array}$$

(2 : 4 : 2′ : 4′-β-chloro-α-truxillic acid), whilst that of hexachloro-α-truxillic acid is

$$\begin{array}{l}(2:4)C_6H_3Cl_2\cdot \underset{|}{C}Cl\cdot \underset{|}{C}H\cdot CO_2H \\ \qquad\qquad CO_2H\cdot CH\cdot CCl\cdot C_6H_3Cl_2(2':4')\end{array}.$$

A. McK.

Veratroylformic Acid and its Reduction. L. Vanzetti (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 629—635).—The preparation of veratroylformic acid from dimethylolivil (Körner and Vanzetti, Abstr., 1903, i, 430) is described: it is best purified by means of its bisulphite derivative, crystallises from ether in small, white nodules composed of flexible needles, and melts at 138—139° to a dark brown liquid. In structure, it is 3 : 4-dimethoxybenzoylformic acid, as shown by its formation on oxidising methyleugenol (Tiemann and Matsmoto, Abstr., 1878, 503) and methyl*iso*eugenol (Ciamician and Silber, Abstr., 1890, 966). On fusion with an alkali hydroxide, it is converted into protocatechuic acid, and with chromic acid in acetic acid solution it yields veratric acid. When heated above 200°, it loses carbon dioxide, giving a small quantity of methylvanillin. The *potassium*, *silver*, *barium*, *lead*, and *copper* salts are described.

On reduction with sodium amalgam, veratroylformic acid gives 3 : 4-*dimethoxymandelic acid*, $C_6H_3(OMe)_2\cdot CH(OH)\cdot CO_2H$, which crystallises from benzene in white, lustrous plates, melts at 105°, and slowly decomposes on exposure to light, giving a resin containing methylvanillin; it undergoes a slight decomposition in the same sense when crystallised from various solvents. The *alkali* salts crystallise from alcohol, and the *silver* salt darkens in the air; the *lead* and *copper* salts are also described. W. A. D.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XII. Esterification of Phthalonic and Homophthalic Acids. Rudolf Wegscheider and Arthur Glogau (*Monatsh.*, 1903, 24, 915—958. Compare Abstr., 1900, i, 657; 1902, i, 617, 620).—Methyl alcohol and hydrogen chloride convert phthalonic acid into methyl phthalonate, $C_{11}H_{10}O_5$, crystallising from methyl alcohol in rhombic plates [$a:b:c = 0{\cdot}9137:1:1{\cdot}0106$] and melting at 66—68° (compare Zincke and Breuer, Abstr., 1885, 269), and *methyl hydrogen phthalonate*, $C_{10}H_8O_5,H_2O$, melting at 79—81°; the anhydrous ester melts at 74—85° undergoing partial decomposition. The same esters are obtained when phthalonic acid is heated with methyl alcohol at 100°, or when silver phthalonate or potassium hydrogen phthalonate reacts with methyl iodide. Sulphuric acid and methyl alcohol convert phthalonic acid into phthalic acid and methyl phthalate. Diazomethane forms the same esters. The partial hydrolysis of methyl phthalonate with hydrogen chloride or potassium hydroxide also forms the same methyl hydrogen phthalonate, and all attempts to prepare an isomeride were thus unsuccessful.

Homophthalic acid reacts with hydrogen chloride and methyl alcohol, forming methyl homophthalate and b-*methyl hydrogen homo-*

phthalate, $CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2Me$, crystallising from ether in thin tablets and melting at 96—98°, dissolving readily in ether, methyl alcohol, or benzene, sparingly in light petroleum. The same ester is obtained on heating homophthalic acid or homophthalic anhydride with methyl alcohol, and is probably present in the mixture obtained by the action of sodium methoxide on homophthalic anhydride in methyl alcohol solution.

The isomeric a-*methyl hydrogen homophthalate*,

$$CO_2Me{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H,$$

is obtained on heating potassium hydrogen homophthalate with methyl iodide, by the action of diazomethane on homophthalic acid, and by the partial hydrolysis of methyl homophthalate with potassium hydroxide, and in small quantity from silver homophthalate and methyl iodide. It crystallises from benzene in transparent tablets and melts at 143—145°, dissolving readily in alcohol or ether, sparingly in light petroleum or cold water.

b-Ethyl hydrogen homophthalate is prepared in similar manner (compare Wislicenus, Abstr., 1886, 879).

The *b*-methyl ester reacts with concentrated ammonium hydroxide, forming phenylacetamide-*o*-carboxylic acid, which is converted by bromine and potassium hydroxide into *benzylamine*-o-*carboxylic acid*, $C_8H_9O_2N$, melting at 217—220° after repeated recrystallisation from water. On heating for some time slightly above the melting point, phthalimidine is formed by loss of water.

The *a*-methyl ester reacts slowly with ammonium hydroxide, forming *benzamide-2-acetic acid*, $NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$, decomposing slightly at 190°, completely at 230°. C. H. D.

Isomeric *m*-Nitrobenzaldoximes. HEINRICH GOLDSCHMIDT (*Ber.*, 1904, **37**, 180—184. Compare Abstr., 1890, 1262; and Ciamician and Silber, this vol., i, 162).—It is shown that Ciamician and Silber's compound melting at 95—100° is a mixture of the *syn*- and *anti*-compounds. The pure *syn*-oxime, obtained by the method already described, melts at 118—119°, which is practically the same temperature (121—122°) as the *anti*-compound. This is due to the fact that the *syn*-compound, during the heating, becomes transformed into the *anti*-. If the *syn*-compound is plunged into a bath at 90° or at any higher temperature, it melts, then solidifies, and afterwards melts at 118—119°. The transformation is also brought about to a certain extent when the *syn*-compound is crystallised from benzene. The configurations are in agreement with the relative strengths of the oximes (*Ber.*, 1895, **28**, 2019), and also with the decomposition of the acetate of the *syn*-oxime into acetic acid and a nitrile (Hantzsch, Abstr., 1894, i, 331).

syn-Aldoximes are more readily esterified than the *anti*-isomerides, as was to be expected from the behaviour of *cis*- and *trans*-modifications of monobasic acids [compare Sudborough and Lloyd, Trans., 1898, **73**, 81]. J. J. S.

Synthesis of Aromatic Aldehydes. F. BODROUX (*Compt. rend.*, 1904, **138**, 92—94).—Magnesium phenyl bromide reacts with ethyl orthoformate on prolonged boiling and subsequent treatment with

hydrochloric acid to form benzaldehyde, according to the following equations: $MgPhBr + OEt{\cdot}CH(OEt)_2 = Mg(OEt)Br + CHPh(OEt)_2$, $CHPh(OEt)_2 + H_2O + HCl = 2CH_3{\cdot}CH_2{\cdot}OH + HCl + CHPhO$, and the yield is 90 per cent. of that required by theory.

A yield of 65 per cent. of *p*-tolualdehyde can similarly be obtained from magnesium *p*-tolyl bromide and ethyl orthoformate, whilst only 20 per cent. of phenylacetaldehyde is obtained by the action of magnesium benzyl chloride on ethyl orthoformate.

Iodoform and bromoform react energetically with magnesium phenyl bromide at the ordinary temperature to yield, among other products, triphenylmethane; the yield is, however, never greater than one-fourth of the theoretical. M. A. W.

Acidimetry of the Hydroxyaldehydes. Hans Meyer (*Monatsh.*, 1903, **24**, 832—839).—Astruc and Murco have shown (Abstr., 1901, i, 66) that certain hydroxyaldehydes react as monobasic acids, and may be titrated with alkali hydroxides in aqueous or alcoholic solution. Piperonal, which does not contain a hydroxyl group, was erroneously included by them, and is found to be entirely neutral. *p*-Hydroxybenzaldehyde and protocatechuic aldehyde behave as monobasic acids, requiring one equivalent of alkali for neutralisation, and vanillin requires only slightly less. *o*-Hydroxybenzaldehyde requires less alkali for neutralisation, and *m*-hydroxybenzaldehyde much less. *iso*Vanillin is neutral (Wegscheider, Abstr., 1883, 190), and the proportions necessary to obtain a good yield in the methylation of protocatechuic aldehyde are given. C. H. D.

Ethers and Homologues of Phloroglucinolaldehyde [2:4:6-Trihydroxybenzaldehyde]. Josef Herzig and Franz Wenzel (*Monatsh.*, 1903, **24**, 857—880. Compare Abstr., 1901, i, 473; 1902, i, 463).—[With E. Kerényi.]—No ether is obtained when hydrogen chloride is passed into a solution of 2 : 4 : 6-trihydroxybenzaldehyde or its aldimide in methyl alcohol, condensation taking place. Diazomethane forms the dimethyl ether, 6-*hydroxy*-2 : 4-*dimethoxybenzaldehyde*, which crystallises from light petroleum in white plates and melts at 70—71°, dissolving readily in organic solvents, insoluble in water. 2 : 6-*Dihydroxy*-4-*methoxybenzaldehyde* could not be prepared by direct methylation, but is obtained when hydrogen cyanide and hydrogen chloride react with phloroglucinol methyl ether and the resulting imide is boiled with water, and crystallises in white needles 3—4 cm. long, decomposing at 170°. Diazomethane forms the dimethyl ether, but a third methyl group cannot thus be introduced. Sodium and methyl iodide, however, react forming 2 : 4 : 6-*trimethoxybenzaldehyde*, melting at 118°.

2 : 4 : 6-Trimethoxybenzaldehyde does not form a coumarin derivative with acetic anhydride, but yields a *triacetyl* derivative crystallising in plates and melting at 122—123°, and a *penta-acetyl* derivative melting at 155—156°.

[With H. Gehringer.]—2 : 4 : 6-Trimethoxybenzaldehyde may also be obtained by the action of hydrogen cyanide and hydrogen chloride on phloroglucinol trimethyl ether, the aldimide thus formed being boiled with water. The *oxime*, $C_6H_2(OMe)_3{\cdot}CH{:}NOH$, crystallises

from methyl alcohol in white needles and melts at 201—203°. 2 : 4 : 6-Trimethoxybenzaldehyde condenses with malonic acid in presence of pyridine, forming 2 : 4 : 6-*trimethoxycinnamic acid*, $C_6H_2(OMe)_3\cdot CH:CH\cdot CO_2H$, crystallising from methyl alcohol in yellowish-white, silky needles melting and decomposing at 218°. Methyl iodide forms the *methyl* ester, white needles melting at 134—135°.

Trimethoxybenzaldehyde condenses with acetone in presence of sodium hydroxide, forming 2 : 4 : 6-*trimethoxybenzylideneacetone*, $C_6H_2(OMe)_3\cdot CH:CH\cdot COMe$, crystallising from light petroleum in yellow scales, softening at 112°, and melting at 118—120°. Condensation with formaldehyde forms white, hygroscopic needles of *methylenebis*-2 : 4 : 6-*trimethoxybenzaldehyde*, $CH_2[C_6H_2(OMe)_3\cdot CHO]_2$, melting at 154—155°.

Potassium permanganate oxidises phloroglucinolaldehyde trimethyl ether in alkaline solution to 2 : 4 : 6-trimethoxybenzoic acid. The *ethyl* ester crystallises from light petroleum in long, thin needles and melts at 77—78°.

[With E. Kerényi.]—*Methylphloroglucinolaldehyde* [2 : 4 : 6-*trihydroxy*-3-*methylbenzaldehyde*], $C_6HMe(OH)_3\cdot CHO$, prepared from methylphloroglucinol by Gattermann's synthesis, crystallises from water with $\frac{1}{2}H_2O$, and after drying at 100° dissolves readily in alcohol, glacial acetic acid, or ethyl acetate, sparingly in ether or water, insoluble in benzene, light petroleum, or chloroform. The *oxime* forms slightly yellow crystals and begins to decompose at 140°, melting to a black mass at 170°. The *penta-acetyl* derivative, $C_6HMe(OAc)_3\cdot CH(OAc)_2$, crystallises from alcohol in white leaflets and melts at 144—145°.

Dimethylphloroglucinolaldehyde [2 : 4 : 6-*trihydroxydimethylbenzaldehyde*], $C_6Me_2(OH)_3\cdot CHO$, prepared in a similar manner from dimethylphloroglucinol, crystallises from ethyl acetate in almost white crystals and decomposes at 190°. The *oxime* forms colourless crystals, insoluble in benzene, light petroleum, or chloroform, dissolving readily in ethyl acetate, ether, or methyl alcohol, and melts at 168°. The *penta-acetyl* derivative, $C_6Me_2(OAc)_3\cdot CH(OAc)_2$, forms white leaflets and melts at 152—153°.

C. H. D.

Δ^2-Keto*cyclo*hexene Derivatives. James B. Garner (*Amer. Chem. J.*, 1904, 31, 143—153).—4-*Hydroxyketo*-3 : 4-*diphenyl*-5-*cumyl*-Δ^2-cyclo*hexene*, $CO<\begin{matrix}CH\text{———}CPh\\CH_2\cdot CH(C_6H_4\cdot CHMe_2)\end{matrix}>CPh\cdot OH$, obtained by the condensation of benzoin with cumylideneacetone in presence of sodium ethoxide, crystallises in long, slender, white needles, melts at 231°, and is readily soluble in hot benzene, glacial acetic acid, or chloroform; its *oxime* melts at 221—223°. When this ketone is boiled with excess of acetic anhydride or acetyl chloride, it is converted into 3 : 4-diphenyl-5-cumylphenyl *acetate*, which crystallises in groups of long needles and melts at 98°. 3 : 4-*Diphenyl*-5-*cumylphenol*,

$$C_6H_4Pr^{\beta}\cdot C_6H_2Ph_2\cdot OH,$$

prepared by hydrolysing the acetate, forms white needles, melts at 155° and is readily soluble in chloroform, benzene, or ether.

4-*Hydroxyketo*-3 : 4-*diphenyl*-5-*anisyl*-Δ^2-cyclo*hexene*,

$$CO<\begin{matrix}CH\!=\!=\!=\!=\!=\!=\!=\!=\!=CPh\\ CH_2\cdot CH(C_6H_4\cdot OMe)\end{matrix}>CPh\cdot OH,$$

prepared by the condensation of benzoin with anisylideneacetone, crystallises in needles, melts at 233·5°, is soluble in hot benzene or chloroform, and gives a red coloration with concentrated sulphuric acid; its *oxime* melts at 196°. 3 : 4-*Diphenyl*-5-*anisylphenol* is a crystalline substance which melts at 159—160°, and is readily soluble in ether, benzene, chloroform, or acetic acid; its *acetate* melts at 141—142°.

4-*Hydroxyketo*-3 : 4-*diphenyl*-5-*piperyl*-Δ^2-cyclo*hexene*,

$$CO<\begin{matrix}CH\!=\!=\!=\!=\!=\!=\!=\!=\!=CPh\\ CH_2\cdot CH(C_6H_3{:}O_2{:}CH_2)\end{matrix}>CPh\cdot OH,$$

formed by the condensation of benzoin with piperonyleneacetone, crystallises in slender, white, lustrous needles, melts at 240°, is soluble in hot chloroform, and sparingly so in hot benzene or alcohol; its *oxime* melts at 190—191°.

4-*Hydroxyketo*-5-*phenyl*-3 : 4-*dicumyl*-Δ^2-cyclo*hexene*,

$$CO<\begin{matrix}CH{:}C(C_6H_4\cdot CHMe_2)\\ CH_2\!-\!-\!-\!-\!-\!-\!-CHPh\end{matrix}>C(OH)\cdot C_6H_4\cdot CHMe_2,$$

obtained by the condensation of cuminoin with benzylideneacetone, crystallises from glacial acetic acid, melts at 214°, and is soluble in ethyl acetate, chloroform, or hot benzene; its *oxime* melts at 208°. 5-*Phenyl*-3 : 4-*dicumylphenol* crystallises in large, thin plates, melts at 137°, and is soluble in ethyl acetate, benzene, chloroform, or ether; its *acetate* melts at 122°.

4-*Hydroxyketo*-5-*phenyl*-3 : 4-*dianisyl*-Δ^2-cyclo*hexene*,

$$CO<\begin{matrix}CH{:}C(C_6H_4\cdot OMe)\\ CH_2\!-\!-\!-\!-\!-CHPh\end{matrix}>C(OH)\cdot C_6H_4\cdot OMe,$$

prepared by the condensation of anisoin with benzylideneacetone, crystallises in white needles, melts at 207°, and is soluble in benzene, alcohol, acetic acid, or chloroform. The 1 : 5-*diketone*, formed as the first product of this reaction, melts at about 168—174°. E. G.

Behaviour of *p*-Aminoacetophenone towards Aldehydes. MAX SCHOLTZ and L. HUBER (*Ber.*, 1904, **37**, 390—397).—*p*-Aminoacetophenone contains two groups which are reactive towards aldehydes, the amino-group undergoing condensation in alcoholic solution, and the methyl group adjoining carbonyl condensing in presence of potassium hydroxide. Most aromatic aldehydes undergo both condensations simultaneously in presence of potassium hydroxide, but in the case of aldehydes containing phenolic hydroxyl, the addition of alkali is without effect, only the amino-condensation taking place.

p-Aminoacetophenone and benzaldehyde form a *compound*,

$$CHPh{:}N\cdot C_6H_4\cdot CO\cdot CH{:}CHPh,$$

crystallising from pyridine in yellow needles and from glacial acetic acid in red needles, both forms melting at 143—144°. Boiling dilute hydrochloric acid hydrolyses it to *ω-benzylidene-*p*-aminoacetophenone hydrochloride*, $CHPh{:}CH\cdot CO\cdot C_6H_4\cdot NH_3Cl$, crystallising in colourless needles, decomposed by water or by heat. p-*Benzylideneaminoaceto-*

phenone, $CHPh{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$, from *p*-aminoacetophenone and benzaldehyde in neutral solution, crystallises from alcohol in colourless needles and melts at 96°. *p*-Tolualdehyde and *p*-aminoacetophenone in presence of potassium hydroxide form the *compound*,

$$C_6H_4Me{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4Me,$$

crystallising from pyridine in yellow needles and melting at 188°; with hydrochloric acid, it forms $C_6H_4Me{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}NH_3Cl$. *p*-Aminoacetophenone and piperonal in alkaline solution form the *compound*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2$, crystallising from pyridine in yellow needles and melting at 189°. Acetic acid removes 1 mol. of piperonal on warming, yielding the *compound*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2$, which forms red needles melting at 198—200°. The *isomeride*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$, is formed by the condensation of *p*-aminoacetophenone with piperonal in neutral solution, and melts at 147°. Cinnamaldehyde forms yellow needles of the *compound*,

$$CHPh{:}CH{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CHPh,$$

melting at 191°. Cuminaldehyde forms yellow needles of the *compound*, $C_6H_4Pr{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4Pr$, melting at 128°; anisaldehyde forms yellow leaflets of the *compound*,

$$OMe{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe,$$

melting at 191°. The condensation products from *m*- and *p*-nitrobenzaldehydes, $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$, crystallise from pyridine in felted, yellow needles melting at 195°, and brick-red, microscopic needles melting at 191—193° respectively. Salicylaldehyde and *p*-aminoacetophenone, with or without the addition of potassium hydroxide, form only the *compound*,

$$OH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3,$$

crystallising from alcohol in glistening, orange needles and melting at 116°. *p*-Hydroxybenzaldehyde reacts in similar manner, the product melting at 209°. Vanillin also yields only the *compound*,

$$OMe{\cdot}C_6H_3(OH){\cdot}CH{:}N{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3,$$

which forms yellow (or red) needles melting at 167°. In alkaline solution, furfuraldehyde forms an oil which is converted into the compound, $(C_4H_3O{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2)_2,H_2SO_4$, by cold dilute sulphuric acid. Formaldehyde and *p*-aminoacetone in neutral solution form the compound $CH_2(NH{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3)_2$, crystallising from alcohol in colourless needles and melting at 188°. C. H. D.

Additive Compounds derived from *o*-Benzoquinone. C. Loring Jackson and Horace C. Porter (*Amer. Chem. J.*, 1904, 31, 89—119. Compare Abstr., 1903, i, 266).—Tetrabromo-*o*-quinone readily unites with various substances with the formation of additive compounds. When it is left in contact with such a substance for several days at the ordinary temperature, the product consists of 2 mols. of tetrabromo-*o*-quinone combined with 1 mol. of the other substance. These compounds crystallise in white needles or prisms and are stable at the ordinary temperature, but are decomposed by heat with formation of hexabromo-*o*-quinocatechol ether; they are all

soluble in solution of sodium hydroxide. The following is a list of these *compounds*, designated as α-compounds, and the temperatures at which they suffer decomposition: $2C_6O_2Br_4,H_2O$, 190—200°; $2C_6O_2Br_4,MeOH$, 178—182°; $2C_6O_2Br_4,CH_2Ph\cdot OH$, 165—170°; $2C_6O_2Br_4,CH_3\cdot CO_2H$, 220—230°. When the methyl alcohol compound is heated with strong hydrochloric acid at 100° for 30 hours, it yields a compound melting at 185—187°, which is probably tetrabromocatechol, together with chloroform, chlorine, and possibly bromine. By the action of hydrobromic acid on the benzyl alcohol compound, benzylidene bromide, bromine, and probably benzyl bromide and tetrabromocatechol are produced; hydrochloric acid acts in a similar manner. If the benzyl alcohol compound is boiled with sulphuric acid of sp. gr. 1·38, hexabromo-*o*-quinocatechol ether is obtained.

Another series of compounds, termed β-compounds, is obtained from the α-compounds. The methyl alcohol β-compound is formed when the α compound is boiled with methyl alcohol, whilst the water and benzyl alcohol compounds are produced by the action of acetic anhydride and dry sodium acetate on the corresponding α-compounds. These β-compounds crystallise in white, polygonal plates, are very stable, and melt without undergoing decomposition. The following are the *compounds* which have been prepared, and their melting points: $2C_6O_2Br_4,MeOH$, 261°; $2C_6O_2Br_4,CH_2Ph\cdot OH$, 216—217°; $2C_6O_2Br_4,H_2O$, 222°.

The first product of the action of methyl alcohol on tetrabromo-*o*-benzoquinone is not the α-compound, but a *substance*, probably $3C_6O_2Br_4,MeOH$, which crystallises in small, red prisms and melts at 192—193°. The *acetyl* derivative of the methyl alcohol β-compound, $2C_6O_2Br_4,CH_3\cdot CO_2Me$, crystallises in needles and melts at 249°. By the action of acetic anhydride on the benzyl alcohol β-compound, a *substance*, $C_6O_2Br_4,CH_3\cdot CO_2\cdot CH_2Ph$, is produced, which forms greyish-white crystals and melts at 208—209°. When the benzyl alcohol α-compound is reduced with zinc and acetic acid, a *compound*, $2C_6H_2O_2Br_4,CH_2Ph\cdot OH$, is obtained, which crystallises in pale yellow needles, melts at 273—274°, and yields a *triacetyl* derivative melting at 275—280°.

Toluene and acetophenone unite with tetrabromo-*o*-quinone forming two red *substances*, $C_6O_2Br_4,C_6H_5Me$ and $C_6O_2Br_4,C_6H_5\cdot COMe$, melting at 70—75° and 50—60° respectively, which, on exposure to air, gradually lose the volatile constituent; it therefore appears that these substances are merely tetrabromo-*o*-quinone with toluene or acetophenone of crystallisation. When tetrabromo-*o*-quinone is boiled with acetophenone, triphenylbenzene is produced.

It has been stated previously (Jackson and Koch, Abstr., 1901, i, 597—598) that by the action of glacial acetic acid on tetrabromo-*o*-quinone, hexabromo-*o*-quinocatechol is produced, but it is now found that this substance was formed indirectly by the action of alcohol on the crude product. The white additive compound of acetic acid obtained by Jackson and Koch (*loc. cit.*) is apparently related to the β-series, since it is formed when the α-compound is heated with acetic acid.

When tetrabromo-*o*-benzoquinone is heated at 130—150°, it undergoes decomposition with formation of hexabromo-*o*-quinocatechol ether and a white *substance* melting at 180—190°. The quinone is decomposed by boiling water with production of hydrogen bromide and hexabromo-*o*-quinocatechol ether. Fuming nitric acid dissolves the quinone forming a purple coloured solution from which, on diluting with water, the quinone is reprecipitated unchanged. E. G.

2-Substitution Derivatives of Anthraquinone. FELIX KAUFLER (*Ber.*, 1904, **37**, 59—66).—The following compounds were prepared from 2-aminoanthraquinone through the diazo-reaction (compare this vol., i, 207). 2-*Iodoanthraquinone* crystallises from alcohol in light yellow needles, melts at 175—176°, and boils at 290—300° under 15 mm. pressure; on nitration, it gives remarkably stable nitro-derivatives, and does not lose iodine when boiled with methyl-alcoholic potassium methoxide. 2-Bromoanthraquinone, prepared by converting anthraquinone-2-diazonium bromide into its perbromide and decomposing this at 200°, crystallises from amyl alcohol and melts at 204—205°; Graebe and Liebermann (*Annalen*, 1870, Supt.-Band., 7, 279) have described 2-bromoanthraquinone as melting at 187°. 2-Chloroanthraquinone melts at 208—209°, not at 204°, as stated by Graebe and Rée (Trans., 1886, **49**, 531). 2-*Nitroanthraquinone*, prepared by decomposing anthraquinone-2-diazonium nitrate with sodium copper nitrite according to Hantzsch and Blagden's method (Abstr., 1900, i, 704), crystallises from glacial acetic acid in bright yellow, lustrous needles, melts at 184—185°, and boils without decomposing; on reduction, it regenerates 2-aminoanthraquinone. 2-Nitroanthraquinone differs from the 1-nitro-compound in not being attacked by boiling aniline or *p*-toluidine, although resembling it in undergoing conversion into 2-*methoxyanthraquinone* when heated with methyl-alcoholic potassium methoxide; the product crystallises from alcohol in long, bright-yellow needles and begins to sublime at about 100°. W. A. D.

Anthraquinone-1-sulphonic Acids. ROBERT E. SCHMIDT (*Ber.*, 1904, **37**, 66—72).—A claim for priority for the discovery that on sulphonating anthraquinone in presence of mercury or its salts, α- and not β-sulphonic acids are obtained (compare Iljinsky, this vol., i, 176); the process has been patented by Friedrich Bayer & Co. Details are given for preparing anthraquinone-1-sulphonic acid and 1 : 5- and 1 : 8-disulphonic acids both by direct sulphonation and by the action of sodium sulphite on 1-nitro, 1 : 5-, and 1 : 8-dinitroanthraquinones. The latter process is also employed for preparing anthraquinone-1 : 6- and -1 : 7-disulphonic acids from Claus's α- and β-nitroanthraquinonesulphonic acids respectively.

When the 1-anthraquinonesulphonic acids are heated at a high temperature with ammonia or primary amines, the corresponding amino- or alkylamino-anthraquinones which have already been described are obtained (compare Abstr., 1903, i, 498, 839). When heated with methyl-alcoholic potassium hydroxide, the analogous methoxyanthraquinones are produced, and with a solution of potassium

phenoxide in an excess of phenol, anthraquinone-1-sulphonic acid gives the hitherto unknown *phenoxyanthraquinone.*

On reduction with zinc dust and ammonia, anthraquinone-1-sulphonic acid gives anthracene-1-sulphonic acid, which, on fusion with potassium hydroxide, is converted into *α-anthrol.* The latter crystallises from acetic acid on diluting with water in yellow leaflets and melts at 152°.

On oxidation with 80 per cent. sulphuric anhydride at 30—35°, the same sulphonic acid gives a new *purpurinsulphonic acid* (1 : 2 : 4-*trihydroxyanthraquinone*-5- or -8-*sulphonic acid*). On nitration, the 1-sulphonic acid gives a mixture of 5-*nitro-* and 8-*nitro-anthraquinone*-1-*sulphonic acids,* which are easily separated; the former crystallises from the concentrated acid and the latter separates on diluting with water. On reducing the nitro-acids with aqueous sodium sulphide, the sodium salts of 5- and 8-*aminoanthraquinone*-1-*sulphonic acids* are obtained; these can be diazotised and coupled with phenols and with amines. On heating the aminoanthraquinonesulphonic acids with lime-water at a high temperature, 5- and 8-*amino*-1-*hydroxyanthraquinones* are obtained; with methylamine, 1-*methylamino*-5- and -8-*aminoanthraquinones* are produced. 5- and 8-*Methylaminoanthraquinone*-1-*sulphonic acids* are obtained by heating the foregoing nitrosulphonic acids with aqueous methylamine at 50—70°; at a higher temperature (150—170°), 1 : 5- or 1 : 8-*dimethyldiaminoanthraquinones* are the products. W. A. D.

Action of Nitric Acid on Cyclic Ketones. I. Action of Nitric Acid on the Ketones, $C_{10}H_{16}O$, of the Terpene Series. Michael I. Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 953—962).—The action of nitric acid of sp. gr. 1·075 and 1·1 on fenchone in sealed tubes at 120—130° leaves nearly the whole of the fenchone unchanged, only small quantities of the following two products being obtained: (1) a *secondary nitrofenchone,* $C_{10}H_{15}(NO_2)O$, which is soluble in alkali hydroxide solution and separates from light petroleum solution in long, thin needles melting at 86—87°; the nitro-group is reduced to NH_2 by means of tin and hydrochloric acid. (2) A *tertiary nitrofenchone,* probably

$$\begin{array}{l} CH_2\cdot CH\text{—}CMe\cdot NO_2 \\ \mid \quad\; CMe_2 \;\mid \\ CH_2\cdot CH\text{—}CO \end{array}$$

, which is insoluble in alkali hydroxide solution and separates from light petroleum solution in monoclinic, pearly scales or prisms melting at 96·5—97·5°. With tin and hydrochloric acid, it yields a small quantity of the amino-compound, together with the corresponding *hydroxyfenchone,* $C_{10}H_{15}O\cdot OH$, which has the sp. gr. 1·0071 at 25°/0°, and n_D 1·4636 at 25°; it is readily soluble in ether, but only slightly so in water.

The action of nitric acid of sp. gr. 1·075 on pulegone at 80—90° gives products soluble, and others insoluble, in alkali hydroxide solution. Of the latter, four were isolated: (1) a *compound* $C_{10}H_{15}O\cdot NO_2$, which melts at 123° and yields the corresponding amino-derivative on reduction, and (2) three compounds of the

composition $C_{10}H_{16}O(NO_2)_2$, and melting at 96—98°, 84—86°, and 64—72° respectively; the one melting at 84—86° is obtained also by the action of nitrogen peroxide on a light petroleum solution of pulegone.

With nitric acid of sp. gr. 1·075, dihydrocarvone acts readily at 80° and carvenone at 85—90° yielding nitro-derivatives; the unattacked portions do not undergo isomeric change.

From these results and those previously obtained (Abstr., 1896, i, 177), the author draws the following conclusions: (1) the ketones, $C_{10}H_{16}O$, of the terpene series having a saturated character—camphor and fenchone—react with dilute nitric acid with comparative difficulty. The presence of the grouping -CHMe facilitates the action, fenchone reacting more readily than camphor. (2) Those ketones of the terpene series which have an unsaturated character react very readily with dilute nitric acid; with pulegone, combination takes place at the double linking. (3) Under the conditions employed in the author's experiments, dilute nitric acid does not bring about isomeric change in cyclic ketones. (4) In general, cyclic ketones behave towards dilute nitric acid in the same way as towards hydrocarbons. T. H. P.

Chemically Pure α- and β-Ionones, their Separation, and Hydrogen Sulphite Compounds. PHILIPPE CHUIT (*Chem. Centr.*, 1904, i, 280—281; from *Rev. gén. Chim. pure appl.*, 1903, 6, 422—435). —The oxime of ψ-ionone, prepared in the ordinary way, boils at 185—190° under 16 mm. and at 190—195° under 20 mm. pressure, and it has the sp. gr. 0·938. By treating the oxime with phosphoric acid of sp. gr. 1·742 (compare Abstr., 1902, i, 722), a product boiling at 172—178° under 175 mm. pressure is obtained; the main portion of the liquid boils at 174—175° and consists for the most part of α-iononeoxime together with a small quantity of β-iononeoxime. By the action of a 70 per cent. solution of sulphuric acid on ψ-iononeoxime at the ordinary temperature, almost pure β-ionone is obtained. The isomeric change is not so readily effected by means of the phenylhydrazone.

In order to separate α- and β-ionone sodium hydrogen sulphites, the former is salted out by adding sodium chloride to the warm solution of these compounds. The α-compound separates in leaflets which have a nacreous lustre. The β-compound remains in solution or when present in large quantity separates as an oil; on evaporation small crystals are formed.

α-Ionone sodium hydrogen sulphite, $C_{13}H_{21}O\cdot SO_3Na,1\frac{1}{2}H_2O$, crystallises from water in white leaflets or from alcohol in monoclinic rhombs, is readily soluble in hot alcohol, only slightly so in ethyl acetate, and insoluble in benzene; the ketone group of the ionone is not combined with the sulphite group.

The *oxime* of α-ionone sodium hydrogen sulphite is readily soluble in water and appears to yield the free oxime when distilled from an alkaline solution with steam. When α-ionone oxime is dissolved in sodium hydrogen sulphite solution, α-ionone sodium hydrogen sulphite and not the oxime compound is formed. The *semicarbazone sodium*

hydrogen sulphite, $SO_3Na\cdot C_{13}H_{21}:N\cdot NH\cdot CO\cdot NH_2$, crystallises from boiling alcohol in slender, white needles and is readily soluble in water; by the action of sodium hydroxide, it appears to form the free semicarbazone of α-ionone and not α-ionone itself. Dilute sulphuric acid precipitates the free *acid* from its aqueous solution; it forms white leaflets and melts and decomposes at 203°. The *phenylhydrazone* of α-ionone sodium hydrogen sulphite appears to form α-ionone hydrazone when treated with sodium hydroxide; the latter does not dissolve in boiling sodium hydrogen sulphite solution.

When α-ionone sodium hydrogen sulphite is evaporated with a 50 per cent. solution of sulphuric acid in a vacuum at 30—35°, a residue is left which is soluble in ethyl acetate but insoluble in benzene. The solution yields a syrupy residue which has a strong acid reaction and the sp. gr. 1·21 at 15°; the *sodium* salt, $C_{13}H_{21}O\cdot SO_3Na$, forms regular, transparent crystals and is very sparingly soluble in ethyl acetate. The *potassium* salt is also anhydrous. A second stable *acid*, $C_{13}H_{21}O\cdot SO_3H,3H_2O$, may be prepared by evaporating an aqueous solution of α-ionone sodium hydrogen sulphite with sulphuric acid to dryness on the water-bath or by heating the salt with a 50 per cent. solution of sulphuric acid for a short time at 60°; it is readily soluble in alcohol, ether, ethyl acetate, or water, but less so in warm benzene, and melts and decomposes at 80—88°. By the action of sodium hydroxide on this acid, α-ionone is not formed, but only the *sodium* salt, $C_{13}H_{21}O\cdot SO_3Na,3H_2O$, and by the action of concentrated sulphuric acid it loses sulphur dioxide and yields an oil. This salt may also be obtained directly from the salt $C_{13}H_{21}O\cdot SO_3Na,1\frac{1}{2}H_2O$ by the action of sulphuric acid, by boiling the alcoholic solution with ethyl bromide, or by heating the alcoholic solution with a drop of concentrated sulphuric acid. The *semicarbazone*,

$$SO_3Na\cdot C_{13}H_{21}:N\cdot NH\cdot CO\cdot NH_2,3H_2O,$$

crystallises from ethyl acetate in white needles. Attempts to prepare the oxime and hydrazone failed. The *potassium* salt, $C_{13}H_{21}O\cdot SO_3K,3H_2O$, crystallises in white leaflets.

β-Ionone sodium hydrogen sulphite, $C_{13}H_{21}O\cdot SO_3Na,2H_2O$, prepared by dissolving β-ionone in a boiling solution of sodium hydrogen sulphite, is more soluble in cold than in hot water and separates from its solution on the addition of sodium chloride as an oil which has a sp. gr. 1·200 at 15°; it crystallises from a concentrated aqueous solution and is readily soluble in ethyl acetate, acetone, or benzene. The *semicarbazone*, $SO_3Na\cdot C_{13}H_{21}:N\cdot NH\cdot CO\cdot NH_2,4H_2O$, forms small lustrous tablets and is soluble in warm water, but only sparingly so in ethyl acetate. The *oxime* separates as an oil on the addition of sodium chloride. The *calcium hydrogen sulphite compound* of *β-ionone*, $(C_{13}H_{21}OSO_3)_2Ca,4H_2O$, is much less soluble than the sodium compound, and when decomposed by sodium hydroxide gives a theoretical yield of β-ionone.

Chemically pure α- and β-ionones have been prepared from their sodium hydrogen sulphite compounds. The odour of the former is more delicate and penetrating than that of the ordinary preparation and somewhat resembles that of iris, whilst β-ionone has more the true violet odour. α-Ionone boils at 127·6° under 12 mm., at

131·1° under 13, at 131·8° under 14, and at 134·3° under 16 mm. pressure; it has sp. gr. 0·9338 at 15°, 0·9301 at 20°, and n_D 1·50048 at 16·5° and 1·50001 at 17·2°. A kilogram of water dissolves 0·0935 parts of α-ionone. β-Ionone boils at 134·6° under 12 mm., at 136·8° under 13 mm., at 137·9° under 14 mm, and at 140·4° under 16 mm. pressure; it has sp. gr. 0·9488 at 15°, 0·9442 at 20°, and n_D 1·52070 at 16·8° and 1·52008 at 17·5°.

When β-ionone is boiled with a solution of *p*-bromophenylhydrazine in glacial acetic acid for an hour, the ordinary *p*-bromophenylhydrazone melting at 116° is not formed, but an isomeride which melts at 166—167° (compare Tiemann, Abstr., 1895, i, 530). Since the melting point of α-ionone-*p*-bromophenylhydrazone is not altered by treatment in this way, the reaction may be used to detect the presence of β-ionone. By boiling β-iononephenylhydrazone with glacial acetic acid, a *compound* which crystallises from methyl alcohol and melts at 121° is obtained.

α-Iononesemithiocarbazone, $C_{13}H_{20}\colon N\cdot NH\cdot CS\cdot NH_2$, melts at 121° and is readily soluble in benzene; by the action of phthalic acid and steam, α-ionone is slowly regenerated. *β-Iononesemithiocarbazone* crystallises from dilute alcohol, melts at 158°, is readily soluble in benzene or alcohol, and is quickly decomposed by phthalic acid. Ironesemithiocarbazone, after repeated crystallisation from benzene and light petroleum, melts at 181°. E. W. W.

Chemically Pure α- and β-Ionones. DE LAIRE & Co. (*Chem. Centr.*, 1904, i, 282; from *Rev. gén. Chim. pure appl.*, 6, 471—473).—The ionone patents are discussed in connection with Chuit's work (see preceding abstract). Chuit's method of separating α- and β-ionones is not better than Tiemann's. E. W. W.

Menthone, Camphorphorone, and Pinophorone. FRIEDRICH W. SEMMLER (*Ber.*, 1904, 37, 234—241).—*Benzylidenementhonehydroxylamine* [*α-Hydroxylaminobenzylmenthone*],

$$CH_2<\begin{matrix}CH_2\cdot CHMe\\ CHPr^\beta-CO\end{matrix}>CH\cdot CHPh\cdot NH\cdot OH,$$

crystallises from light petroleum in needles melting at 162°, which, on reduction with sodium and alcohol, is converted into *α-aminobenzylmenthol*, $CH_2<\begin{matrix}CH_2\text{———}CHMe\\ CHPr^\beta\cdot CH(OH)\end{matrix}>CH\cdot CHPh\cdot NH_2$, an oil boiling at 202—206° under 15 mm. pressure, has a sp. gr. 1·013 at 20°, and n_D 1·5255.

Benzylmenthol is an oil boiling at 179—180° under 9 mm. pressure, which has a sp. gr. 0·9904 at 20° and n_D 1·5255, forming, on oxidation with chromic acid in acetic acid solution, *benzylmenthone*, $C_{17}H_{24}O$, an oil boiling at 175—180° under 10 mm. pressure, which has a sp. gr. 0·981 at 20°, n_D 1·515, and does not form an oxime.

Dihydrocamphoryl alcohol, $CHPr^\beta<\begin{matrix}CH(OH)-\\ CH_2\cdot CH_2\end{matrix}>CHMe$, obtained on reducing camphorphorone, boils at 185—192°, has a sp. gr. 0·899 at 20°, n_D 1·4604, and has the odour of menthol. The *phenylurethane* crystallises in needles from methyl alcohol melting at 82°, the *acetate* boils at 92—94° under 14 mm. pressure, has a sp. gr. 0·930, and n_D

1·432. When heated with oxalic acid, an unsaturated hydrocarbon, "*anhydrocamphoryl alcohol*," [1-*methyl*-3-iso*propyl*-Δ^1-cyclo*pentene*] $\mathrm{CHPr^{\beta}}\left\langle\begin{matrix}\mathrm{CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\right\rangle\mathrm{CMe}$, is obtained, which boils at about 144—146°, has a sp. gr. 0·801 at 20°, and n_D 1·4478 ; it unites with two atoms of bromine.

Dihydrocamphorone, $\mathrm{CHPr^{\beta}}\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\right\rangle\mathrm{CHMe}$, formed by the oxidation of the preceding alcohol with chromic acid, is an oil which boils at 184—185°, has a sp. gr. 0·887, and n_D 1·4389 ; the *semicarbazone* melts at 196—197° and the *oxime* at 79°. On oxidation with permanganate, two ketonic acids are formed and can be separated by means of their semicarbazones. One acid boils at 166—168° under 14 mm. pressure, has a sp. gr. 1·0214, n_D 1·4488, and forms a *semicarbazone* melting at 167—168° and an *oxime* melting at 75° ; as on further oxidation, α-methylglutaric acid is formed, it must have the formula $\mathrm{COPr^{\beta}{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H}$.

The other ketonic acid, which boils at 156° under 14 mm. pressure and forms a semicarbazone melting at 140°, has the formula $\mathrm{CO_2H{\cdot}CHPr^{\beta}{\cdot}CH_2{\cdot}CH_2{\cdot}COMe}$, since it is easily converted into α-*iso*propylglutaric acid.

Pinophorone, $\mathrm{CH_2{:}CMeCH}\left\langle\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\right\rangle\mathrm{CO}$, is produced, together with acetone and a hydrocarbon, C_9H_{14}, on distilling the calcium salt of pinonic acid. It boils at 203—205°, has a sp. gr. 0·9284, n_D 1·4805, and forms a *semicarbazone* melting at 157—158°, and with hydroxylamine an oxime which was not isolated, as in contact with mineral acids it is converted into a *piperidone*, $C_9H_{15}ON$, which boils at 136—140° under 14 mm. pressure, has a sp. gr. 0·9904 and n_D 1·5014, whilst on reduction with sodium and alcohol *pinocamphoryl alcohol*, $C_9H_{16}O$, is obtained; this boils at 203°, has a sp. gr. 0·921 at 20°, and n_D 1·483.

The *hydrocarbon*, C_9H_{14}, obtained at the same time as pinophorone, boils at 140°, has a sp. gr. 0·8142 at 20°, and n_D 1·4628. E. F. A.

[Interaction of Mercuric Acetate with Terpenes and Compounds containing the C_3H_5 Group.] A Correction. LUIGI BALBIANO and VINCENZO PAOLINI (*Ber.*, 1904, 37, 225).—The compound previously described by the authors (this vol., i, 73) as hydroxyapiole is apiol, and that described as the benzoyl derivative of hydroxyapiole is a mixture of apiole and benzoic anhydride. A. McK.

Phylloerythrin, a new Derivative of Chlorophyll. LÉON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1903, 638—642).—*Phylloerythrin*, obtained by extracting with cold chloroform the fresh excrement of a cow, fed entirely on grass, separates from this solvent in crystals, which are brownish-red with a tinge of violet when seen in mass. Solutions of phylloerythrin in acetic acid or chloroform give absorption spectra showing four bands, but the spectrum of the former solution is considerably modified by the addition of hydrochloric acid. Sulphuric acid dissolves phylloerythrin, forming a grass-green solution, the spectrum of which shows several bands, which are ill-defined with the exception of one in the red. In several respects, phylloerythrin

resembles scatocyanin (Schunk, Abstr., 1902, i, 301), but is distinguished by the absorption spectra of its solutions, illustrations of which are given in the original. T. A. H.

Composition of Furfuraldehyde-phloroglucide. W. GOODWIN and BERNHARD TOLLENS (*Ber.*, 1904, **37**, 315—319).—Furfuraldehyde-phloroglucide probably has the composition $C_{11}H_8O_4$, but prolonged drying in the air results in a small increase in weight and a considerable decrease in the percentage of carbon (calc. 64·7, found, 63·9, 62·8, 61·9), probably owing to oxidation with liberation of carbon dioxide; a sample dried during $2\frac{1}{2}$ hours in a current of hydrogen gave carbon 65·1 per cent., and after $3\frac{1}{2}$ hours 64·5 per cent. T. M. L.

Synthesis of Nencki and Sieber's "Resacetein." CARL BÜLOW and CONST. SAUTERMEISTER (*Ber.*, 1903, **37**, 354—368. Compare Abstr., 1881, 811, and 1903, i, 357).—Resacetein, $C_{16}H_{12}O_4$, or 7-hydroxy-2-*op*-dihydroxyphenyl-4-methylene-1 : 4-benzopyranol,

$$OH\cdot C_6H_3<\begin{matrix}\text{———O———}\\ C(:CH_2)\cdot CH\end{matrix}>C\cdot C_6H_3(OH)_2,$$

can be synthesised by condensing 2 : 4-diethoxybenzoylacetone with resorcinol and subsequently hydrolysing the ethoxy-groups in the condensation product.

2 : 4-Diacetoxybenzoylacetone forms a *copper* salt crystallising in greyish-green plates melting at 171°, which, when hydrolysed with dilute sulphuric acid, is converted into diethoxybenzoylacetone.

Benzeneazo-2 : 4-*diethoxybenzoylacetone*,

$$NPh:N\cdot CH(COMe)\cdot CO\cdot C_6H_3(OEt)_2,$$

crystallises in glistening needles melting at 82—83° and easily soluble in organic solvents.

5-op-*Diethoxyphenyl*-3-*methyl*iso*oxazole*, $\begin{matrix}CMe\cdot CH\\ \|\qquad\quad\\ N\text{———}O\end{matrix}>C\cdot C_6H_3(OEt)_2$,

crystallises from alcohol in long, silk, glistening needles melting at 126·5°.

The *hydrochloride* of *resacetein diethyl ether* is formed on condensing diethoxybenzoylacetone and resorcinol in presence of hydrogen chloride; on heating, it blackens at 205—210° and melts and decomposes at 235°. The free base crystallises in glistening, red needles which melt between 77° and 81° and form a *picrate* separating in dark golden-yellow needles melting and decomposing at 235°, a *sulphate* ($+2H_2O$) melting at 215—217°, and a *platinichloride*,

$$(C_{20}H_{20}O_4)_2,H_2PtCl_6,$$

which separates in microscopic, orange-yellow needles.

8-*Nitroso*-7-*hydroxy*-2-op-*diethoxyphenyl*-4-*methylene*-1 : 4-*benzopyranol* forms microscopic crystals with a bronze-like lustre melting between 170° and 178°, dissolves in sulphuric acid with a bluish-violet, and in alkali with a dark red coloration. 7-*Acetoxy*-2-op-*diethoxyphenyl*-4-*methylene*-1 : 4-*benzopyranol* crystallises in glistening, red, hexagonal plates, dissolves in sulphuric acid forming a dark yellow solution which has a green fluorescence, and melts to a gummy mass between 228° and 242°.

7-*Hydroxy*-2-op-*diethoxyphenyl*-4-*methyl*-1 : 4-*benzopyran*,

$$OH\cdot C_6H_3<\begin{matrix}\text{———O———}\\ CHMe\cdot CH\end{matrix}>C\cdot C_6H_3(OEt)_2,$$

formed on reducing the free base with zinc dust and acetic acid, is a colourless, amorphous substance which, on heating, darkens at 118° and melts between 125° and 147°. The 7-*acetoxy*-derivative, which has marked electrical properties, sinters at about 100° and melts at 118° to a gummy mass.

Resacetein, in every way identical with Nencki and Sieber's compound (*loc. cit.*), is best prepared from the diethoxyphenylmethylenebenzopyranol by heating it in sealed tubes with hydrochloric acid between 150° and 180°. The synthetical product forms a triacetate, $C_{22}H_{18}O_7$, identical with that described by Rasinsky (Abstr., 1882, 1288). When slowly distilled with aqueous sodium hydroxide, diethoxyphenylmethylenebenzopyranol is resolved into resorcinol and resacetophenone diethyl ether. E. F. A.

Condensations of Cotarnine and Hydrastinine with Ketones. CARL LIEBERMANN and F. KROPF (*Ber.*, 1904, 37, 211—216).—*Anhydrocotarnineacetone*, prepared by the condensation of cotarnine with acetone, is formulated either as

$$CH_2{:}O_2{:}C_6H(OMe)<\begin{matrix}CH(CH_2{\cdot}COMe){\cdot}NMe \\ CH_2\text{———————}CH_2\end{matrix}$$

or $CH_2{:}O_2{:}C_6H(OMe)(CH{:}CH{\cdot}COMe){\cdot}CH_2{\cdot}CH_2{\cdot}NHMe$, according as $CH_2{:}O_2{:}C_6H(OMe)<\begin{matrix}CH(OH){\cdot}NMe \\ CH_2\text{———}CH_2\end{matrix}$ or the tautomeric formula is accepted for cotarnine. It separates from aqueous acetone in honey-coloured prisms and melts at 83°; it is distinguished from cotarnine by its insolubility in excess of aqueous sodium hydroxide solution. Its *hydrochloride* forms silky needles and melts and decomposes at 171°. Its *methiodide* melts at 144°.

Anhydrohydrastinineacetone, $CH_2{:}O_2{:}C_6H_2<\begin{matrix}CH(CH_2{\cdot}COMe){\cdot}NMe \\ CH_2\text{———————}CH_2\end{matrix}$ or $CH_2{:}O_2{:}C_6H_2(CH{:}CH{\cdot}COMe){\cdot}CH_2{\cdot}CH_2{\cdot}NHMe$, prepared from hydrastinine and acetone, melts at 72°. Its *platinichloride* melts at 196—198°.

Anhydrocotarninemethyl propyl ketone, $C_{17}H_{23}O_4N$, prepared from cotarnine and methyl propyl ketone, melts at 86—92°. *Anhydrocotarnine-acetophenone*, $C_{20}H_{21}O_4N$, prepared from cotarnine and acetophenone, separates from alcohol in colourless prisms and melts at 126°. *Anhydrohydrastinine-acetophenone*, $C_{19}H_{19}O_3N$, crystallises in prisms and melts at 74°. A. McK.

Cytisine. MARTIN FREUND (*Ber.*, 1904, 37, 16—23. Compare Abstr., 1901, i, 288).—Cytisoline, $C_{11}H_{11}ON$, the chief product of the reduction of cytisine with phosphorus and hydriodic acid, melts at 199° and not at 192° as previously stated. It is oxidised by chromic acid to *cystolinic acid*, $C_{11}H_9O_3N$, which crystallises from acetic acid in minute needles, the melting point of which lies above 350°; it has acid properties, dissolves readily in ammonia, and is precipitated by acids. Nitric acid gives a *nitrocytisoline*, $C_{11}H_{10}O_3N_2$, which separates from alcohol in yellow crystals, sinters at 240°, and melts at 275°. Reduction with sodium in alcohol converts cytisolin into *a-cytisolidine*,

$C_{11}H_{15}N$, a coniine-like base which forms a *platinichloride* melting at 216° and a picrate melting at 228—229°.

An isomeride of cytisolidine to which the name of *β-cytisolidine* is given is produced as a by-product in the preparation of cytisoline; the *platinichloride* crystallises from alcohol and hydrochloric acid and melts at 207°; the *hydrochloride* forms small, silky needles and melts at 250—260°; the *picrate* crystallises from alcohol in needles and sinters at 225—228°. T. M. L.

Epinephrine and its Degradation Products. JOHN J. ABEL (*Ber.*, 1904, 37, 368—381. Compare Abstr., 1899, i, 395; 1903, i, 278; also Jowett, Trans., 1904, 85, 192).—When oxidised with nitric acid, epinephrine yields oxalic acid and a substance containing nitrogen, which forms a yellow, crystalline, hygroscopic derivative with iodine trichloride and an *aurichloride*, $C_3H_4ON_2,HAuCl_4$, crystallising in prisms. The nitrogen compound, $C_3H_4ON_2$, is held to be a pyrazolone derivative; alkalis react with it forming methylamine. Analytical evidence is adduced in favour of the formula $C_{10}H_{13}O_3N,\frac{1}{2}H_2O$ for epinephrine, and the results obtained by previous workers are discussed. E. F. A.

Synthesis of Ethyl 2:5-Dimethylpyrrole-3-monocarboxylate. IWAN P. OSSIPOFF and G. KORSCHUN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 630—635).—Ethyl 2:5-dimethylpyrrole-3-carboxylate may be obtained by the action of aqueous ammonia on ethyl 2:5-hexadione-3-carboxylate (ethyl αβ-diacetylpropionate), or, in better yield, by using alcoholic ammonia under a high pressure (150°). It forms rhombic crystals (see Knorr, Abstr., 1885, 994). T. H. P.

Synthesis of Trialkylpyrrolemonocarboxylic Compounds. G. KORSCHUN (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 635—636).—*Ethyl 1:2:5-trimethylpyrrole-3-carboxylate*, prepared by the action of methylamine on ethyl diacetylpropionate in the cold, is soluble in alcohol, benzene, and other organic solvents, and separates from aqueous alcohol in long, acicular crystals, melts at 48°, and is volatile in a current of steam. The corresponding *acid* decomposes, without melting, at about 175°.

Ethyl 2:5-dimethyl-1-ethylpyrrole-3-carboxylate is a viscid, yellow liquid, which has a sp. gr. 1·0122 at 24°/15°, boils at 286° (uncorr.) under 748 mm. pressure, and exhibits normal cryoscopic behaviour in benzene. The corresponding *acid*, when heated, does not melt, but decomposes, yielding 2:5-dimethyl-1-ethylpyrrole.

2:5-Dimethyl-1-butylpyrrole-3-carboxylic acid, obtained by hydrolysing the product of the action of normal butylamine on ethyl diacetylpropionate, forms a white, crystalline mass which melts at 154°, dissolves in alcohol, and, to a less extent, in benzene, and in the latter shows normal cryoscopic behaviour. T. H. P.

Synthesis of Ethyl 1:2:5-Trimethylpyrrole-3-carboxylate. G. KORSCHUN and TREFILIEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 636).—This compound (see preceding abstract) may be obtained free

from ethyl 2 : 4 : 5-trimethylpyrrole-3-carboxylate by the action of methyl iodide on potassium 2 : 5-dimethylpyrrole-3-carboxylate.

T. H. P.

Derivatives of 2-Picolyl- and 2-Picolylmethyl-alkine. I. Karl Löffler (*Ber.*, 1904, 37, 161—174).—2-Picolylalkine [2-β-hydroxyethylpyridine] (Ladenburg, Abstr., 1898, i, 687) reacts with fuming hydriodic acid and red phosphorus (compare Koenigs and Hoppe, Abstr., 1902, i, 394) when heated in a sealed tube at 120—130°, forming an iodide, $C_5H_4N\cdot CH_2\cdot CH_2I$, a volatile oil giving an irritating vapour and dissolving sparingly in water, readily in alcohol or ether. The *picrate*, $C_7H_8NI,C_6H_3O_7N_3$, crystallises from benzene in short, highly refractive prisms and melts at 111—112°. The *platinichloride*, $(C_7H_8NI)_2,H_2PtCl_6$, is a dark red, crystalline precipitate melting and decomposing at 149—150°.

Heating converts the iodo-base into a solid isomeride having the constitution of a pyridinium iodide, $\begin{array}{l} CH\cdot CH:C-CH_2 \\ \| \qquad\quad\ | \quad\ \ | \\ CH\cdot CH:NI\cdot CH_2 \end{array}$, crystallising from water in slightly yellow needles and melting at 211—213°.

Hydrobromic acid and red phosphorus convert 2-β-hydroxyethylpyridine into a *bromide*, $C_5NH_4\cdot C_2H_4Br$, which may be isolated as a volatile, colourless oil by distillation with steam. The *platinichloride*, $(C_7H_8NBr)_2,H_2PtCl_6$, is a flesh-coloured, amorphous precipitate melting at 171—172° ; the *picrate* crystallises from benzene in yellow rosettes and melts at 95—96°. The base passes gradually into the isomeric pyridinium bromide, which forms long needles containing $1H_2O$; the dried salt melts at 226—227° and dissolves readily in cold water, very sparingly in alcohol. Moist silver oxide precipitates silver bromide ; the filtrate is alkaline and red in colour. Potassium iodide precipitates the crystalline iodide from a solution of the bromide. Moist silver chloride forms the chloride, crystallising from alcohol in prisms containing H_2O, and melting, when dry, at 175°. The *platinichloride*, $(C_7H_8NCl)_2PtCl_4$, is an amorphous powder.

Alkylamines react at 100° with the volatile bromo-base to form alkylaminoethylpyridines. Diethylamine forms *2-β-diethylaminoethylpyridine*, $C_5H_4N\cdot C_2H_4\cdot NEt_2$, a colourless liquid boiling at 115—116° under 13 mm. pressure and having an odour of nicotine. The *hydrochloride* is a white, deliquescent powder melting at 172—173° ; the *platinichloride*, $C_{11}H_{18}N_2,H_2PtCl_6$, forms thin, golden leaflets and melts and decomposes at 226° ; the *aurichloride* forms small, yellow crystals and melts at 184°. The *normal picrate* melts at 163—164° and the readily soluble *basic picrate* at 96—97°. The *mercurichloride* crystallises in needles and melts at 103—104°.

2-β-Methylaminoethylpyridine, $C_5H_4N\cdot C_2H_4\cdot NHMe$, from methylamine, is a colourless base boiling at 113—114° under 30 mm. pressure. The *platinichloride*, $C_8H_{12}N_2,H_2PtCl_6,2H_2O$, forms very large, orange needles ; the *aurichloride*, small, yellow needles, melts and decomposes at 205° ; the *normal picrate*, glistening needles, melts at 193—194°, and the *basic picrate*, hexagonal prisms, at 137—138°.

Alcoholic ammonia at 125° converts the bromo-base into *2-β-amino-*

ethylpyridine, $C_5H_4N{\cdot}C_2H_4{\cdot}NH_2$, boiling at 92—93° under 12 mm. pressure, colouring litmus blue, and fuming with hydrochloric acid. The *hydrobromide* crystallises from alcohol in glistening, almost colourless leaflets and melting at 129°. The *platinichloride* separates from water in long needles containing $2H_2O$, and melts and decomposes at 232—233°. The *picrate* forms long, slender needles and melts at 215—216°. 2-β-*Acetylaminoethylpyridine*, $C_5H_4N{\cdot}C_2H_4{\cdot}NHAc$, is a viscid oil boiling at 175°. Attempts to produce condensation to an *iso*quinoline derivative were unsuccessful.

Together with the primary base, a secondary base, $(C_5H_4N{\cdot}C_2H_4)_2NH$, is obtained, boiling at 192° under 8 mm. pressure and possessing strongly marked basic properties. The *hydrochloride* crystallises from alcohol in small needles, the *platinichloride*, $(C_{14}H_{17}N_3)_23H_2PtCl_6,2H_2O$, forms small, orange needles; the *picrate*, long, yellow needles, melts at 181—183°, and the *mercurichloride*, glistening leaflets, at 121—122°. Nitrous acid forms a *nitroso*-derivative, $(C_5H_4N{\cdot}C_2H_4)_2N{\cdot}NO$, a slightly red oil. The *platinichloride* forms orange needles.

2-Picolylmethylalkine [β-hydroxy-2-propylpyridine],

$$C_5H_4N{\cdot}CH_2{\cdot}CHMe{\cdot}OH$$

(Ladenburg, *loc. cit.*), also reacts with hydriodic acid, forming the iodo-base, a volatile oil, passing slowly into a crystalline isomeride. The *platinichloride*, $(C_8H_{10}NI)_2,H_2PtCl_6$, forms groups of reddish-brown needles and melts and decomposes at 152—153°. C. H. D.

Indole Dyes. Martin Freund [with Gustav Lebach] (*Ber.*, 1904, 37, 322—323. Compare Abstr., 1903, i, 278).—The following substances have been obtained by condensing 2-methylindole with aldehydes. p-*Dimethylaminobenzylidenebis-2-methylindole methiodide*,

$$CH(C_9H_8N)_2{\cdot}C_6H_4{\cdot}NMe_3I,$$

white needles melting at 181—182°. o-*Hydroxybenzylidenebis-2-methylindole*, $CH(C_9H_8N)_2{\cdot}C_6H_4{\cdot}OH$, white needles melting at 230—231°. o-*Hydroxybenzylidene-2-methylindole hydrochloride*,

$$HCl,C_9H_7N{:}CH{\cdot}C_6H_4{\cdot}OH,$$

red flakes melting at 202°. o-*Nitrobenzylidenebis-2-methyl-1-ethylindole*, $CH(C_9H_7NEt)_2{\cdot}C_6H_4{\cdot}NO_2$, white needles melting at 229°. o-*Chloro*-p-*dimethylaminobenzylidenebis-2-methyl-1-ethylindole*,

$$CH(C_9H_7NEt)_2{\cdot}C_6H_3Cl{\cdot}NMe_2,$$

white needles melting at 219°. *Valerylenebis-2-methylindole*,

$$CH(C_9H_8N)_2{\cdot}C_4H_9,$$

white needles melting at 157°. *Piperonylenebis-2-methylindole*,

$$CH(C_9H_8N)_2{\cdot}C_6H_3{:}CH_2O_2,$$

white needles melting at 213°. *Piperonylene-2-methylindolehydrochloride*, $HCl,C_9H_7N{:}CH{\cdot}C_6H_3{:}CH_2O_2$, reddish-brown, glistening scales melting at 194°. *Piperonylenebis-2-methyl-1-ethylindole*,

$$CH(C_9H_7NEt)_2{\cdot}C_6H_3{:}CH_2O_2,$$

white needles melting at 175°. T. M. L.

Action of Organomagnesium Compounds on Alkylated Phthalimides. Franz Sachs and Al. Ludwig (*Ber.*, 1904, 37, 385—390).—Magnesium does not react with ω-bromoalkylphthalimides, and the synthesis of amino-alcohols by this means is therefore

impossible. Magnesium alkyl haloids, however, react with alkylphthalimides, and the results obtained are in accordance with those obtained by Béis (this vol., i, 15) and Bouveault (this vol., i, 13).

Magnesium methyl bromide reacts with ethylphthalimide at low temperatures, forming *3-hydroxy-3-methyl-2-ethyl*iso*indolinone*,

$$C_6H_4<\begin{matrix}CO\\CMe(OH)\end{matrix}>NEt,$$

which crystallises from water below 70° in leaflets, and melts and decomposes at 93—94°, dissolving readily in most solvents and separating with difficulty. *3-Hydroxy-2 : 3-diethyl*iso*indolinone*,

$$C_6H_4<\begin{matrix}CO\\CEt(OH)\end{matrix}>NEt,$$

from magnesium ethyl bromide, forms rhombic crystals and melts at 129—130°. Ethylphthalimide and magnesium phenyl bromide form *3-hydroxy-3-phenyl-2-ethyl*iso*indolinone*, which crystallises from dilute acetone or alcohol in prismatic needles and melts at 166—167°. Hydrochloric acid at temperatures not higher than 120° forms the *hydrochloride*, crystallising from water in hexagonal prisms and melting at 189°. Further heating with hydrochloric acid at 160—170° causes hydrolysis, with the formation of *o*-benzoylbenzoic acid.

The reaction takes place differently in the case of benzoicsulphinide which is otherwise closely related to phthalimide. Ethylbenzoicsulphinide and magnesium ethyl bromide form a *compound*, $C_{13}H_{21}O_3NS$, probably $OH\cdot CEt_2\cdot C_6H_4\cdot SO_2\cdot NHEt$, crystallising from ether in large, acute rhombohedra and melting at 99—100°. The *compound* from ethylbenzoicsulphinide and magnesium phenyl bromide, $C_{21}H_{21}O_3NS$, crystallises from alcohol and melts at 184—185°, dissolving in concentrated sulphuric acid to an intense yellowish-red solution, in accordance with its representation as a derivative of triphenylcarbinol. C. H. D.

1 : 8-Dimethyltetrahydroquinoline. MARTIN FREUND (*Ber.*, 1904, 37, 22—23).—This compound was synthesised because it appeared probable that it might be identical with cytisolidine (see this vol., i, 263).

1 : 8-*Dimethyltetrahydroquinoline*, $C_9NH_9Me_2$, boils at 238—240° (uncorr.); the *platinichloride* forms small, stout, yellow needles and decomposes at 223°; the *picrate* crystallises from 96 per cent. alcohol in small, yellowish-red, rhombic tablets and melts at 160°.

T. M. L.

Benzidine Isomerism. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 667—675).—In the action of hydrochloric acid on hydrazobenzene, yielding benzidine and *iso*benzidine, the author considers that the strong mineral acid, in aqueous or alcoholic solution, tends to the formation of a stronger base, that is, to the transformation of tervalent into quinquevalent nitrogen. In cases where the hydrogen chloride does not exhibit its acid properties, owing to non-ionisation, as, for example, in benzene solution, such a transformation does not take place.

The author's experiments show that when azobenzene in acetic acid

solution is saturated with hydrogen bromide, it yields benzidine, 2 : 4-dibromoaniline, and *p*- and *o*-bromoaniline; a similar reaction occurs with hydrogen chloride, but hydrogen iodide undergoes oxidation with liberation of iodine.

These results point to the quinonoid structure of azobenzene, so that nearly all pigments can be referred to the quinone type.

T. H. P.

Interaction of Zinc Ethyl and Benzenediazonium Chloride. II. Ethylation of Benzidine. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 675—678. Compare Abstr., 1903, i, 441).—In the author's previous paper (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 155; *loc. cit.*), he gave the melting point 116° to *s*-diethylbenzidine, whilst Hofmann (*Annalen*, 1860, **115**, 365) described under this name a compound melting at 65°. The author has now prepared the latter compound, which he finds to consist of a mixture of about 85 per cent. of *s*-diethylbenzidine with 15 per cent. of tetraethylbenzidine, which melts at 90°.

T. H. P.

Degradation of Dihydroxytetramethylrosaminesulphonic Acid. CARL LIEBERMANN and A. GLAWE (*Ber.*, 1904, **37**, 203—210. Compare Liebermann, Abstr., 1903, i, 860).—When dihydroxytetramethylrosaminesulphonic acid, $\begin{array}{l} \quad O\text{——}C_6H_3{=}NMe_2{\cdot}O \\ NMe_2{\cdot}C_6H_3{\cdot}C{\cdot}C_6H_2(OH)_2{\cdot}SO_2 \end{array}$, is boiled with aqueous potassium hydroxide for 1—2 hours, the resulting oil is a mixture of tetramethyldiaminoxanthone, $\begin{array}{l} \quad O\text{——}C_6H_3{\cdot}NMe_2 \\ NMe_2{\cdot}C_6H_3{\cdot}CO \end{array}$, and tetramethyldiaminoxanthen, $\begin{array}{l} \quad O\text{——}C_6H_3{\cdot}NMe_2 \\ NMe_2{\cdot}C_6H_3{\cdot}CH_2 \end{array}$, which may be separated by glacial acetic acid.

Tetramethyldiaminoxanthone crystallises in needles and melts at 240°, whilst tetramethyldiaminoxanthene also forms needles and melts at 113°. The identity of those compounds with the substances prepared by Biehringer from formaldehyde and dimethylaminophenol (Abstr., 1897, i, 73) is established. The platinichlorides of tetramethyldiaminoxanthone and tetramethyldiaminoxanthen also resemble the corresponding compounds prepared by Biehringer.

The presence of tetramethyldiaminoxanthen along with tetramethyldiaminoxanthone and catecholsulphonic acid as products of the hydrolysis of dihydroxytetramethylrosaminesulphonic acid is shown to be due to the presence in the dihydroxytetramethylrosaminesulphonic acid used of a small amount of its leuco-derivative.

The fact that the degradation of dihydroxytetramethylrosaminesulphonic acid can be effected with so much greater ease than the corresponding change with rosaniline and methyl-violet, malachite-green, &c., is due to the acidic hydroxyl and sulphonic groupings.

The degradation of tetramethylrosaminesulphonic acid proceeds in an analogous manner; *potassium dimethylaminohydroxybenzophenonemonosulphonate*, prepared by heating an aqueous solution of tetramethylrosaminesulphonic acid with potassium hydroxide, separates in pink leaflets.

A. McK.

Diphenyleneazone Series. FRITZ ULLMANN and PAUL DIETERLE (*Ber.*, 1904, 37, 23—36).—Diphenyleneazone oxide, $\left.\begin{array}{l}C_6H_4\cdot N\\ C_6H_4\cdot N\end{array}\right>O$, prepared by reducing 2 : 2′-dinitrodiphenyl with sodium sulphide, melts at 139° and not at 152° as stated by Täuber (Abstr., 1892, 183). The diphenazone, $\begin{array}{l}C_6H_4\cdot N\\ C_6H_4\cdot N\end{array}$, prepared by reducing with stannous chloride, is purer than that produced by the old method and melts at 156°; the *zincochloride* of the methochloride forms yellow needles, is readily soluble in water and sparingly so in alcohol, and melts at 235°.

3 : 8-*Dimethyldiphenyleneazone oxide*, $\left.\begin{array}{l}C_6H_3Me\cdot N\\ C_6H_3Me\cdot N\end{array}\right>O$, prepared from 2 : 2′-dinitro-4 : 4′-ditolyl, crystallises from benzene in large, clear plates and melts at 209°. 3 : 8-Dimethyldiphenyleneazone, $\begin{array}{l}C_6H_3Me\cdot N\\ C_6H_3Me\cdot N\end{array}$, prepared by the electrolytic reduction of the dinitroditolyl, crystallises from benzene in sulphur-yellow crystals, melts at 188°, and is identical with the compound described by L. Meyer (Abstr., 1893, i, 733); the *nitrate* separates from dilute nitric acid in yellow needles and melts at 166°; the *zincochloride* of the *methochloride*, $(C_{14}H_{12}N_2,MeCl)_2,ZnCl_2$, crystallises in small, yellow needles, melts at 231°, and is readily soluble in water.

3 : 8-Diaminodiphenyleneazone, $\begin{array}{l}NH_2\cdot C_6H_3\cdot N\\ NH_2\cdot C_6H_3\cdot N\end{array}$, prepared by the electrolytic reduction of dinitrobenzidine, crystallises from boiling xylene in stout, dark green crystals, melts at 265°, and is identical with the substance prepared by Täuber (Abstr., 1892, 184).

4 : 4′-*Tetramethyldiaminodiphenyl*, $C_{12}H_8(NMe)_2$, prepared by oxidising dimethylaniline with sulphuric acid and turpentine, crystallises from benzene in colourless flakes and melts at 197°. The 2 : 2′-*dinitro*-derivative crystallises from xylene or acetic acid in garnet-red needles, melts at 229·5°, decomposes at a slightly higher temperature, and is not identical with the substance described by Michler and Pattinson (Abstr., 1884, 747). 3 : 8-*Tetramethyldiaminodiphenyleneazone oxide*, $\left.\begin{array}{l}NMe_2\cdot C_6H_3\cdot N\\ NMe_2\cdot C_6H_3\cdot N\end{array}\right>O$, crystallises from alcohol in radiating groups of carmine-red needles and melts at 242°. 3 : 8-*Tetramethyldiaminodiphenyleneazone* $\begin{array}{l}NMe_2\cdot C_6H_3\cdot N\\ NMe_2\cdot C_6H_3\cdot N\end{array}$, crystallises from xylene in silky, red needles and melts at 270°. The *hydrochloride*, $C_{16}H_{18}N_4,HCl$, separates from hydrochloric acid in bluish-black crystals, melts at 236°, and yields a blue solution in dilute hydrochloric acid. The *nitrate* is a dark blue crystalline powder and melts at 238°.

2 : 2′-*Diamino*-4 : 4′-*tetramethyldiaminodiphenyl*,

$$C_{12}H_6(NH_2)_2(NMe_2)_2,$$

crystallises from a mixture of benzene and light petroleum in colourless flakes and melts at 166°.

4 : 4′-Tetraethyldiaminodiphenyl, $C_{12}H_8(NEt_2)_2$, prepared by oxidising diethylaniline with sulphuric acid and turpentine, is identical with

that prepared by other methods. The 2 : 2′-dinitro-derivative melts at 132° and not at 140° as described by Eppstein. 3 : 8-*Tetraethyldiaminodiphenyleneazone*, $\begin{matrix} NEt_2\cdot C_6H_3\cdot N \\ | \qquad\quad || \\ NEt_2\cdot C_6H_3\cdot N \end{matrix}$, forms glistening, dark crystals which become red when dried on the water-bath and melt at 184°.

6 : 6′-Dinitro-4 : 4′-diamino-3 : 3′-dimethoxydiphenyl

$$C_{12}H_4(OMe)_2(NH_2)_2(NO_2)_2,$$

crystallises from alcohol in red flakes, melts at 222°, and agrees with the properties of the substance described by Starke. 3 : 8-*Diamino-2 : 9-dimethoxydiphenyleneazone*, $\begin{matrix} OMe\cdot C_6H_2(NH_2)\cdot N \\ | \qquad\qquad\quad || \\ OMe\cdot C_6H_2(NH_2)\cdot N \end{matrix}$, prepared by the electrolytic reduction of the nitro-compound, separates from alcohol in dark yellow crystals and melts at 244°. The *hydrochloride*, $C_{14}H_{14}O_2N_4,2HCl$, separates in red crystals with a metallic lustre and begins to lose hydrogen chloride at 105°. T. M. L.

Reactions in the Urazole Series. SALOMON F. ACREE (*Amer. Chem. J.*, 1904, 31, 185—188. Compare Abstr., 1902, i, 242 ; 1903, i 867).—A reply to Wheeler and Johnson (Abstr., 1903, i, 693).

E. G.

1-Phenyl-3 : 5-dithiolurazole. SALOMON F. ACREE and O. W. WILLCOX (*Ber.*, 1904, 37, 184—185. Compare Abstr., 1902, i, 242 ; 1903, i, 867).—*Ethyl phenylthiosemicarbazidecarbothionoxylate*,

$$NH_2\cdot CS\cdot NH\cdot NPh\cdot CS\cdot OEt,$$

obtained by heating ethyl chlorothiocarbonate (Klason, Abstr., 1887, 1029) with phenylthiosemicarbazide in acetone solution, crystallises from alcohol and melts and decomposes at 173°. When boiled for several hours with sodium hydroxide solution and then acidified with hydrochloric acid, it yields 1-*phenyl*-3 : 5-*dithiolurazole*,

$$N\begin{matrix} \nearrow C(SH)\cdot NPh \\ \qquad\qquad | \\ \searrow C(SH):N \end{matrix},$$

melting at 181°. When titrated with alkali, using phenolphthalein as indicator, this behaves as a monobasic acid, and also yields only a *mono*-silver salt. J. J. S.

Carbazoles. E. DELÈTRA and FRITZ ULLMANN (*Arch. Sci. phys. nat.*, 1904, [v], 17, 78—92. Compare Graebe and Ullmann, Abstr., 1896, i, 575, and Ullmann, Abstr., 1898, i, 591).—3 : 4-*o-Tolylaziminobenzoic acid*, $N\begin{matrix} \nearrow N(C_6H_4Me) \searrow \\ \searrow N \text{———————} \nearrow \end{matrix}C_6H_3\cdot CO_2H$, prepared by diazotising 3-amino-4-*o*-tolylaminobenzoic acid (Heidensleben, Abstr., 1891, 306), forms small, acicular crystals, melts at 204°, and is very soluble in alcohol and benzene, less so in ether, and insoluble in boiling water. When heated with twice its weight of lime, it is converted into 1-*methylcarbazole*, $NH\begin{matrix} \nearrow C_6H_3Me \\ \quad | \\ \searrow C_6H_4 \end{matrix}$. This forms white, tabular crystals,

melts at 120°, gives a green colour with sulphuric acid, and is soluble in alcohol or ether, less so in acetic acid, and insoluble in water; the *picrate* forms red needles and melts at 143°.

2-Nitro-4-*p*-tolylaminobenzoic acid, prepared by condensing 4-chloro-3-nitrobenzoic acid with *p*-toluidine (compare Schöpff, Abstr., 1890, 374), on reduction with aluminium and sodium hydroxide furnishes the corresponding *amino*-compound, which crystallises in transparent, lanceolate needles, melts at 183°, and is insoluble in acetic acid and alcohol, less so in ether and benzene. Its solution in ether exhibits a violet fluorescence. On diazotisation, it furnishes 3 : 4-p-*tolylazimino-benzoic acid*, which melts at 267°, is soluble in acetic acid, alcohol, and benzene, less so in ether and light petroleum, and, when distilled with lime, furnishes 3-*methylcarbazole*. This crystallises in white scales, melts at 203°, gives a fugitive green colour with sulphuric acid, which is intensified by the addition of nitric acid, and resembles 1-methylcarbazole in solubility. Its solutions in alcohol, ether, and benzene exhibit a violet fluorescence. The *picrate* forms bright red needles, melts at 180°, and is soluble in alcohol and benzene.

2-*Nitro*-4-m-*xylylaminobenzoic acid*,

$$C_6H_3Me_2\cdot NH\cdot C_6H_3(NO)_2\cdot CO_2H,$$

obtained by condensing *m*-xylidine with 4-chloro-3-nitrobenzoic acid, is a bright red, crystalline powder and melts at 213°. On reduction with aluminium powder, it furnishes the corresponding *amino-acid*, which crystallises in grey masses, melts at 179°, and when diazotised yields 3 : 4-m-*xylylaziminobenzoic acid*,

$$N\lessgtr\!\begin{matrix}N(C_6H_3Me_2)\\ N\text{———————}\end{matrix}\!>C_6H_3\cdot CO_2H;$$

this crystallises from nitrobenzene in rose-tinted prisms, melts at 230°, and is soluble in alcohol and acetic acid. When distilled with lime, it furnishes *p*-methylacridine and 1 : 3-*dimethylcarbazole*. The latter is a white, crystalline powder which melts at 95°, gives a green coloration with sulphuric acid, and is very soluble in alcohol, acetone, and benzene, less so in acetic acid; the *picrate* forms red needles, melts at 188°, and is soluble in alcohol and benzene.

4-Nitro-2-aminodiphenylamine, prepared by reducing dinitrodiphenylamine with sodium sulphide, melts at 134° (compare Nietzki, Abstr., 1895, 164). Its hydrochloride, when diazotised in acetic acid solution, furnishes phenylazimino-4-nitrobenzene,

$$NO_2\cdot C_6H_3<\!\begin{matrix}NPh\\ \text{---}N\end{matrix}\!\gg N,$$

which melts at 168° (compare Nietzki, *loc. cit.*). This does not yield 3-nitrocarbazole on distillation, but on reduction with stannous chloride to phenylazimino-4-aminobenzene and distillation of the latter at 320—330° suspended in paraffin, 3-*aminocarbazole*, $C_{12}NH_8\cdot NH_2$, was obtained. This crystallises in colourless, transparent scales, melts at 254°, gives an azure-blue colour with sulphuric acid, which becomes purple on addition of nitric acid, and is soluble in alcohol and ether; the solutions in these solvents exhibit a violet fluorescence. The *picrate* forms transparent rosettes, becomes yellow and opaque at 100°, and melts and decomposes at about 220°. When diazotised and

condensed with β-naphthol, *p*-aminocarbazole furnishes a red dye of the formula $C_6H_4<\genfrac{}{}{0pt}{}{NH}{C_6H_3\cdot N:N\cdot C_{10}H_6\cdot OH}$. 3-*Acetylaminocarbazole* forms silvery scales, melts at 217°, and is soluble in alcohol and acetic acid, slightly so in ether and benzene.

2 : 4-*Dinitrodiphenylethylamine*, $C_6H_3(NO_2)_2\cdot NEtPh$, obtained by condensing 1-chloro-2 : 4-dinitrobenzene with ethylaniline, forms fine, coral-red, lanceolate crystals, melts at 97·5°, and gives a red colour with sulphuric acid. It is very soluble in benzene, less so in alcohol and ether. When dissolved in alcohol and reduced by ammonium sulphide in presence of ammonia, it yields 4-*nitro-2-aminodiphenylethylamine*, $NO_2\cdot C_6H_3(NH_2)\cdot NEtPh$, which forms dark red crystals, melts at 86·5°, gives a red colour with sulphuric acid, and is readily soluble in acetic acid and alcohol. The *sulphate* forms golden-brown plates and melts at 98°. The diazonium salt resulting from its diazotisation, when warmed in presence of metallic copper, furnishes 3-*nitro-9-ethylcarbazole*, a red, crystalline powder, which melts and decomposes at 108°, gives an intense reddish-violet colour with sulphuric acid, and is readily soluble in acetic acid and benzene, slightly so in alcohol and ether. It does not form a picrate. T. A. H.

Curtius's 4-Bis-3-methylpyrazolone. CARL BÜLOW (*Ber.*, 1904, 37, 91—95).—Curtius's 4-bis-3-methylpyrazolone (Abstr., 1894, i, 247) is in reality 3 : 6-*dimethyldihydropyridazine-4 : 5-dicarboxylic acid cyclohydrazide*, $\begin{array}{l}NH\cdot CMe:C\cdot CO\cdot NH\\ NH\cdot CMe:C\cdot CO\cdot NH\end{array}$; this is shown by the ease with which it loses hydrazine on boiling with dilute acids and by its being formed on boiling ethyl dimethylpyridazinedicarboxylate (Paal and Ubber, Abstr., 1903, i, 290) with alcoholic hydrazine hydrate. It is soluble in both acids and alkalis; the *hydrochloride*, $C_8H_{10}O_2N_4,HCl,H_2O$, forms thick, lustrous needles, and the *tetrabenzoyl* derivative, $C_{36}H_{26}O_6N_4$, prepared by the Schotten-Baumann method, crystallises from hot alcohol in small, broad needles and melts at 189—191°.
W. A. D.

Action of Diazochlorides on Oxalacetic Esters. JULIEN RABISCHONG (*Bull. Soc. chim.*, 1904, [iii], 31, 76—83. Compare Wislicenus and Jensen, Abstr., 1893, i, 146; Favrel, Abstr., 1901, i, 167, and succeeding abstract).—β-Ethyl oxalacetatephenylhydrazone, $NHPh\cdot N:C(CO_2Et)\cdot CO\cdot CO_2Et$, obtained by the action of diazobenzene chloride on ethyl oxalacetate in presence of sodium acetate (compare Wislicenus and Jensen, *loc. cit.*), forms yellowish-red crystals, melts at 72—73°, and is soluble in aqueous solutions of sodium hydroxide or carbonate; when treated with potassium ethoxide, dissolved in alcohol, it appears to form a *potassium* derivative. When the *sodium* derivative, similarly obtained, dissolved in alcohol, is treated with dilute hydrochloric acid, there is precipitated α-*ethyl oxalacetatephenylhydrazone*, which is crystalline and melts at 126—127°.

Methyl oxalacetatephenylhydrazone, similarly prepared, crystallises from xylene and melts at 104—105°.

β-Ethyl oxalacetate-o-tolylhydrazone,

$C_6H_4Me\cdot NH\cdot N{:}C(CO_2Et)\cdot CO\cdot CO_2Et$,

separates from boiling alcohol in yellow crystals and melts at 86—87°. When its *sodium* derivative, dissolved in alcohol, is treated with dilute hydrochloric acid, the *a-isomeride* is precipitated in the course of several days; this crystallises from alcohol and melts at 155—156°. These hydrazones all give a violet coloration with sulphuric acid and potassium dichromate. No hydrazones were obtained by the interaction of oxalacetic esters with the chlorides of diazo-*p*-toluene and diazo-*m*-toluene. T. A. H.

Action of Diazochlorides on Oxalacetic Esters in presence of Alkalis. JULIEN RABISCHONG (*Bull. Soc. chim.*, 1904, [iii], 31, 83—86. Compare preceding abstract).—Ethyl diphenylformazylformate, $NPh{:}N\cdot C(N\cdot NHPh)\cdot CO_2Et$, obtained by the addition of excess of diazobenzene chloride to ethyl oxalacetate, dissolved in alcohol containing sodium hydroxide, melts at 116—117° (compare Bamberger and Wheelwright, Abstr., 1893, i, 84; Wislicenus and Jensen, *ibid.*, 146) and dissolves in an aqueous solution of sodium hydroxide, forming a yellow liquid which becomes violet on addition of acids.

Ethyl o-ditolylformazylformate, similarly prepared, crystallises from anhydrous alcohol, melts at 99—100°, and behaves like its lower homologue with alkalis and acids. T. A. H.

Action of Diazobenzene Chloride on Substituted Hydroxyfumaric Esters. JULIEN RABISCHONG (*Bull. Soc. chim.*, 1904, [iii], 31, 91—96).—The author has regarded the first products of the action of diazobenzene chloride on oxalacetic esters as hydrazones, since by the further action of diazobenzene they are converted into formazyl derivatives (compare two preceding abstracts). It would, however, be possible to explain the formation of the latter if the first products were in reality mixed azo-compounds, thus:

$$NPh{:}N\cdot CH(CO_2Et)\cdot CO\cdot CO_2Et + PhN{:}N\cdot OH = CO_2Et\cdot CO_2H +$$
$$NPh{:}N\cdot CH(N{:}NPh)\cdot CO_2Et \longrightarrow NPh{:}N\cdot C(N\cdot NHPh)\cdot CO_2Et.$$

This investigation has therefore been extended to substituted oxalacetic esters, the ethyl acetoxyfumarate and ethyl a-acetyl-β-hydroxyfumarate simultaneously produced when ethyl sodio-oxalacetate is treated with acetyl chloride (Nef, Abstr., 1893, 629) being employed for this purpose.

When ethyl β-hydroxy-a-acetylfumarate is treated with diazobenzene chloride at 0°, there is formed, not the possible mixed azo-compound, but β-ethyl oxalacetatephenylhydrazone, which, when treated with phenylhydrazine and sodium acetate, dissolved in cold alcohol, is converted into the a-isomeride, but when boiled for several minutes with these reagents furnishes the *diphenyldihydrazone*, which is crystalline and melts at 154—155°.

The products obtained by the action of diazobenzene chloride on oxalacetic esters also reduce alkaline solutions of silver nitrate, which is in favour of the hydrazone constitution assigned to them. When ethyl acetoxyfumarate is treated with diazobenzene chloride in presence of acetic acid, there are formed *ethyl diphenylformazyloxalate*,

NPh:NC:N·NHPh·CO·CO_2Et, and a *substance* which crystallises from benzene, is insoluble in alcohol, and melts at 129—130°. T. A. H.

Action of Alcohols on the Tetrazonium Chlorides derived from Benzidine and *o*-Tolidine J. H. C. Winston (*Amer. Chem. J.*, 1904, 31, 119—142).—When *m*-ditolyltetrazonium chloride is treated with methyl alcohol, *m*-ditolyl is not obtained, but *dimethoxy-m-ditolyl*, $C_{14}H_{12}(OMe)_2$, is produced, which crystallises in silvery leaflets, melts at 145·5°, is soluble in hot alcohol, and yields a *tetranitro*-derivative, melting at 130·5°. By the decomposition of *m*-ditolyltetrazonium chloride with ethyl alcohol, both *m*-ditolyl and diethoxy-*m*-ditolyl are produced. The *tetranitro*-derivative of the latter compound crystallises in rhombs or needles and melts at 142°. If the tetrazonium chloride is treated with sodium methoxide or with a solution of sodium hydroxide in methyl, ethyl, or propyl alcohol, *m*-ditolyl is formed. *m*-Ditolyl is also produced when the tetrazonium chloride is heated with methyl, ethyl, or propyl alcohol in presence of zinc dust, and this reaction affords a good method for its preparation. The action of propyl alcohol on the tetrazonium chloride results in the formation of *m*-ditolyl; no other product could be isolated.

When diphenyltetrazonium chloride is decomposed with methyl alcohol, a trace of diphenyl is formed, but the main product consists of *dimethoxydiphenyl*, which crystallises in pearly plates, melts at 172°, is soluble in hot alcohol, and yields a *tetranitro*-compound melting at 244·6°. By the action of ethyl alcohol, propyl alcohol, or sodium methoxide on diphenyltetrazonium chloride, diphenyl is produced. Diphenyl is also the only product obtained when the tetrazonium chloride is decomposed with methyl, ethyl, or propyl alcohol in presence of zinc dust. E. G.

Method of Separating Albumins from the White of Birds' Eggs. Alexei A. Panormoff (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 690—695. Compare Abstr., 1899, i, 654, 655).—The author describes the methods employed by him for isolating the albumins. In addition to those already published, the following two new ones are given: (1) a quicker separation is obtained by evaporating the solution, not at the ordinary temperature, but at 37—40°. (2) For differentiating albumins, it is proposed: (*a*) to determine the nitrogen content of a given volume of the solution and (*b*) to measure the optical rotation in a 100 mm. tube, and then to calculate what the rotation would be if there were 1 gram of proteid nitrogen in 100 c.c. of the solution. The number thus obtained would be very convenient for determining whether two solutions contained the same or different albumins.

T. H. P.

Stimulating Influence of Proteid Matter on the Oxidation Induced by Manganese. Auguste Trillat (*Compt. rend.*, 1904, 138, 94—96).—The action of a manganous salt in alkali solution as a carrier of oxygen (compare this vol., ii, 38) is largely increased by the addition of a small quantity of proteid matter such as white of egg. The exciting action of the albumin is more apparent at the

beginning of the operation, and falls off with the time, thus in two comparative series of experiments the ratios of the amounts of oxygen absorbed in a given time by gallic acid in an alkaline solution of a manganous salt with and without the addition of egg-albumin were as follows: after 10 minutes, 10; after 32 minutes, 8; after 1 hour, 3·5; after 2 hours, 2·5; after 4 hours, 1·9.

The stimulating influence of albumin on manganese as a carrier of oxygen is to be attributed to its tendency to prevent the precipitation of the manganese dioxide, which is thus maintained in a colloidal state, and is consequently more chemically active.

Beyond a certain limit, an increase in the amount of albumin does not accelerate the oxidation, the maximum effect is produced when one part of albumin is added to 1000 parts of the mixture, and the addition of mercuric chloride, arsenic acid, prussic acid, formaldehyde, &c., has a paralysing effect similar to that observed in the case of solutions not containing albumin. Other proteids, such as horse-serum, and colloids, such as gelatin, dextrin, and gum arabic, have given very variable results. M. A. W.

Enzymes which induce Fermentation isolated from the Cells of the Higher Animals. Julius Stoklasa and F. Czerný (*Ber.*, 1903, **36**, 4058—4069. Compare Abstr., 1903, ii, 320).—The authors show that the juices expressed from muscles, cows' liver, and cows' lungs respectively contain an enzyme which effects the alcoholic fermentation of dextrose and other sugars; it is also shown that the fermentation observed is not due to bacterial action.

The method of obtaining the enzymes in question is described. The freshly prepared juice has very slight glycolytic properties and does not cause alcoholic fermentation. When an antiseptic is not added to the juice, the proteolytic enzymes and bacteria present completely destroy the enzyme which is capable of causing alcoholic fermentation. A mixture of absolute alcohol and ether was added to the cell-free juice, the resulting precipitate being then drained off and dried at 25—30°. After 14 days, the enzymes present in this solid almost entirely lose their property of fermenting sugar.

The freshly prepared solid was added to 10—15 per cent. sterilised aqueous solutions of dextrose, lævulose, galactose, sucrose, maltose, and lactose respectively, thymol (or toluene) being also added to prevent bacterial growth. The amount of carbon dioxide formed was determined after intervals of 12, 36, and 60 hours. The evolution of carbon dioxide was very marked and in many cases started vigorously immediately after the addition of the enzyme. Control experiments conclusively proved that the fermentation observed in the solutions containing thymol or toluene was not induced by bacteria. The enzyme action was found to start and to be completed much more quickly than the bacterial action.

The enzymes, obtained both from plants and animals, can be heated at 100° from 4 to 6 hours without entirely losing their fermenting power.

The solutions were acid in reaction when the fermentation had ceased, lactic acid being one of the products. In the case of an

enzyme prepared from lungs, it is proved, for the first time, that by the anaërobic respiration of animal organs a certain amount of lactic acid is formed. A. McK.

The Reputed Alcoholic Fermentation of Animal Tissues. F. Batelli (*Compt. rend.*, 1903, 137, 1079—1080).—Stoklasa and his pupils claim to have extracted from the tissues of higher animals an enzyme which is capable of inducing alcoholic fermentation (compare Abstr., 1903, ii, 321; this vol, ii, 61). Cohnheim (*Centr. Physiol.*, 17, No. 17) maintains that the fermentation is to be attributed to the presence of micro-organisms, and the results described in this paper support his view. The author finds (1) if 1 per cent. of an antiseptic such as thymol, chloroform, sodium fluoride, potassium arsenite, or salicylic acid is added to the sugar solution containing the extract of the animal tissue no alcoholic fermentation takes place, as Simacek has already shown; (2) if the quantity of the antiseptic is reduced to 0·2 per cent. of sodium fluoride or of salicylic acid, fermentation occurs with the formation of carbon dioxide, alcohol, and butyric acid; (3) the microscopical examination of these fermented solutions reveals the presence of bacteria in the form of mobile rods or chains of cocci. M. A. W.

Amylo-coagulase. A. Boidin (*Compt. rend.*, 1903, 137, 1080—1082. Compare Wolff and Fernbach, this vol., i, 111).—Amylo-coagulase partially precipitates amylase with starch, the precipitated amylase retaining some of its activity. The diastasic activity of the solution diminishes rapidly in consequence of the precipitation of the amylase. N. H. J. M.

Some Organo-magnesium Derivatives of Dihalogen Substituted Aromatic Hydrocarbons. Action of Carbon Dioxide. F. Bodroux (*Bull. Soc. chim.*, [iii], 31, 24—30).—The action of magnesium on the dihalogen derivatives of benzene yields compounds of the type $C_6H_4X{\cdot}MgX$, together with small amounts of a diphenyl halogen derivative. *p*-Dibromobenzene and *p*-chlorobromobenzene yielded magnesium *p*-bromophenyl bromide and magnesium *p*-chlorophenyl bromide respectively. When treated with carbon dioxide, the former of these gave *p*-bromobenzoic acid and di-*p*-bromobenzophenone, which crystallises in colourless plates, melts at 172°, and gives an oxime melting at 150°; the chlorine derivative gave *p*-chlorobenzoic acid and di-*p*-chlorobenzophenone, which forms colourless plates melting at 145°; the *oxime* melts at 135°. S. S.

Organic Chemistry.

Action of Nitric Acid on Acetylene. LUIGI MASCARELLI (*Gazzetta*, 1903, 33, ii, 319—324. Compare Baschieri, Abstr., 1900, 534; 1902, i, 197; Testoni and Mascarelli, Abstr., 1901, i, 494).—The "explosive compound" formed, amongst other substances, on slowly passing acetylene through nitric acid of sp. gr. 1·52, has the composition $C_4H_2O_7N_6$, and, when heated with potassium hydroxide solution, liberates ammonia. On being heated with light petroleum, it decomposes, apparently according to the equation $C_4H_2O_7N_6 = C_4H_2O_3N_4 + N_2O_4$, giving the crystalline substance $C_4H_2O_3N_4$, which has already been described; a small quantity of an oily liquid boiling at 135—140° under 55 mm. pressure is also formed, which, on analysis, gives numbers agreeing with the formula $C_{12}H_{22}O_3N_2$, although the purity of this substance cannot be guaranteed.

The "neutral liquid" formed during the foregoing nitration, after being purified by repeated distillation under diminished pressure, boils at 112° under 40 mm. pressure, and has the composition $C_6H_4O_6N_4$; it is insoluble in acids and alkalis, and evolves ammonia on prolonged heating with aqueous potassium hydroxide.

The monobasic acid, $C_4H_3O_3N$, does not apparently contain the NO_2 group, as it fails to respond to Limpricht's test; it is not reduced by stannous chloride, and does not liberate ammonia with potassium hydroxide. With phenylhydrazine, it gives not a phenylhydrazone, but merely the phenylhydrazine *salt*, $NH_2{\cdot}NHPh,C_4H_3O_3N$, which crystallises from alcohol in white leaflets and melts and decomposes at 176°.

W. A. D.

Action of Reduced Nickel on the Halogen Compounds of the Fatty Series in the Presence of Hydrogen. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1904, 138, 407—409).—A mixture of hydrogen and the vapour of the halogen compound was passed over finely-divided nickel heated at a suitable temperature. The primary alkyl chlorides are attacked at about 250°; as a rule, the first products of reaction are hydrogen chloride and an unsaturated hydrocarbon, but in most instances these unite in the cooler part of the apparatus, giving a small quantity of a tertiary chloride. Thus, *iso*butyl chloride gives hydrogen chloride, *iso*butylene, and *tert.*-butyl chloride; *iso*amyl chloride gives amylene, hydrogen chloride, and the corresponding tertiary chloride. Methyl chloride behaves differently; it gives hydrogen, carbon, and hydrogen chloride. The primary alkyl bromides are attacked at a slightly higher temperature than the chlorides, but the products are analogous. Primary alkyl iodides are decomposed at about 360°, methyl and ethyl iodides giving methane and ethane respectively. Dihalogen derivatives are completely destroyed with formation of carbon, hydrogen, and halogen acid. $\beta\beta$-Dichloropropane behaves differently; it gives a mixture of α- and β-chloropropylenes at

210°. Chloroform gives carbon and hydrogen chloride; carbon tetrachloride yields hexachloroethane as follows: $2CCl_4 + H_2 = C_2Cl_6 + 2HCl$. With a large excess of hydrogen, the hexachloroethane loses halogen, giving tetrachloroethylene, $C_2Cl_6 + H_2 = C_2Cl_4 + 2HCl$; in presence of a still greater excess of hydrogen, carbon and hydrogen chloride are formed. S. S.

Polymerism and Desmotropy of Trimethylethylene Nitrosobromide (β-Bromo-γ-nitroso-β-methylbutane). JULIUS SCHMIDT and FRITZ LEIPPRAND (*Ber.*, 1904, 37, 532—545).—Bis-β-bromo-γ-nitroso-β-methylbutane, $[CMe_2Br\cdot CHMe\cdot NO]_2$, prepared by the action of fuming hydrobromic acid on a mixture of amyl nitrite and amylene, forms glistening, snow-white, rhombic tablets, melts to a bluish-green liquid when rapidly heated to 67°, and can be crystallised from ethyl alcohol or light petroleum if care is taken to start with hot solvent and cool as soon as the nitroso-compound has dissolved. The solutions are at first colourless, but develop a blue colour, gradually at the ordinary temperature, but immediately on warming; after the colour due to depolymerisation has developed, isomeric change sets in and the nitroso-compound soon passes into the colourless *iso*nitroso-compound. Molecular weight determinations in the colourless bis-nitroso-solutions gave M = 386, 375, 359, and 350, calc. 360, but after the colour had developed, the molecular weight in freezing benzene was found to be M = 290. β-Bromo-γ-nitroso-β-methylbutane was obtained only as a blue oil, and attempts at reduction gave much ammonia and very little amine base. *Trimethylethylene* iso*nitrosobromide* [methyl-β-bromo-*iso*propylketoxime], $CMe_2Br\cdot CMe\colon NOH$, can be prepared by heating the nitroso-compound in a thin-walled test-tube over a bare flame until it melts, and then stirring the mass during about 10 minutes with the test-tube in a water-bath at 48°, but if great care is not taken an explosive decomposition takes place; it can also be prepared by boiling a dry ethereal solution of the nitroso-compound until the blue colour has developed and disappeared; the oxime crystallises from light petroleum in stout, white prisms, melts at 78—79°, and decomposes, liberating gas, at 140°; it has a penetrating odour, and does not give Liebermann's reaction, but gives an intense red coloration with ferric chloride. The *benzoyl* derivative, $CMe_2Br\cdot CMe\colon NOBz$, crystallises from alcohol in colourless flakes and melts at 70—71° to a colourless liquid. The p-*nitrobenzoyl* derivative forms glistening, white needles and melts at 105°. The *methyl* ether, $CMe_2Br\cdot CMe\colon NOMe$, prepared by means of diazomethane, forms a pale yellow oil of pleasant odour, which decomposes when distilled even under diminished pressure. The *phenylurethane*, $CMe_2Br\cdot CMe\colon N\cdot O\cdot CO\cdot NHPh$, prepared by the action of phenylcarbimide, crystallises from alcohol in colourless prisms and melts at 88—89°. Hydrochloric acid converts the oxime quantitatively into hydroxylamine hydrochloride and methyl hydroxy*iso*propyl ketone, $HO\cdot CMe_2\cdot COMe$, whilst chlorine, acting on the oxime suspended in cold hydrochloric acid, converts it into βγ-dichloro-γ-nitroso-β-methylbutane, $CMe_2Cl\cdot CMeCl\cdot NO$, a compound which separates in deep blue needles, coloured very much like copper sulphate crystals, melts at 119—120°, and does not appear to exist in a bimolecular form. Potass-

ium hydroxide converts the oxime into a blue oil, which rapidly passes into a colourless mass, the action being apparently that represented by the equation $CMe_2Br\cdot CMe\colon N\cdot OH \rightarrow HBr \rightarrow CMe_2\colon CMe\cdot NO \rightarrow [CMe_2\colon CMe\cdot NO]_x$; the polymeric *γ-nitroso-β-methylbutylene* separates from ethyl acetate as a colourless powder, which softens at 140° and melts at 145° to a colourless liquid. T. M. L.

Tetramethylethylenenitrosobromide [β-Bromo-γ-nitroso-βγ-dimethylbutane]. JULIUS SCHMIDT and FRITZ LEIPPRAND (*Ber.*, 1904, 37, 545—549).—*β-Bromo-γ-nitroso-βγ-dimethylbutane*,

$CMe_2Br\cdot CMe_2\cdot NO$,

forms a powder of the colour of copper sulphate crystals, has a camphor-like and somewhat penetrating odour, is extraordinarily volatile, and when boiled with water partially vaporises, and is partially converted into βγ-dimethyl-Δ^β-butylene, hydrogen bromide, and nitrous acid; it has a normal molecular weight in freezing ethylene dibromide; it does not give Liebermann's reaction, but liberates iodine from potassium iodide, and precipitates silver bromide from alcoholic silver nitrate; under no conditions was it possible to bring about isomeric change, but exposure to sunlight converts it into βγ-dimethyl-Δ^β-butylene dibromide, $CMe_2Br\cdot CMe_2Br$. Cold aqueous potassium hydroxide has no action on the nitroso-compound, but on warming, the original hydrocarbon is regenerated. *βγγ-Tribromo-β-methylbutane* (tribromotrimethylethane), $CMe_2Br\cdot CMeBr_2$, produced by the action of nitrosyl bromide or of bromine on bromomethyl-Δ^β-butylene, crystallises from alcohol in colourless needles, has a strong camphor-like odour, and is so volatile that its melting point could not be determined.

T. M. L.

Trichloro*iso*propyl Alcohol. LOUIS HENRY (*Compt. rend.*, 1904, 138, 205—206).—α-Trichloro*iso*propyl alcohol, readily obtained by Grignard's synthesis from anhydrous chloral and magnesium methiodide (compare Grignard, Abstr., 1901, i, 679), is a white, crystalline substance melting at 50—51°, and boiling at 161·8° under 773 mm. pressure [Thurnlackh, Abstr., 1882, 295, gives 49° and 155° for these constants]. The three alcohols of which this forms the middle term exhibit the same regularity in melting points and boiling points which obtains in other homologous series (compare Abstr., 1901, i, 128; 1903, i, 2; ii, 8). M. A. W.

Action of Sulphuric Acid on Butane-1:3-diol. FRIEDRICH BAUER (*Monatsh.*, 1904, 25, 1—11).—The action of dilute sulphuric acid on β-butylene glycol (butane-αγ-diol) in a sealed tube at 190° yields the following products:—(1) *n*-Butaldehyde. (2) Methyl ethyl ketone; these two compounds are to be expected, according to Lieben's rule (Abstr., 1902, i, 336) for the action of dilute sulphuric acid on glycols in which the two alcohol chains are separated by a hydrocarbon group. (3) As main product, a *compound*, $C_8H_{14}O$, obtained as a yellow liquid boiling at 98—105° under 20 mm. pressure, and under the ordinary pressure at 175—185° with slight decomposition; it is readily soluble in ether and slightly so in water, and unites with 2 atoms of bromine; with zinc ethyl, it yields a dark yellow oil boiling

at about 170° and having an unpleasant odour; its *oxime*, $C_8H_{15}ON$, is a yellow liquid boiling at 180°. (4) A *compound*, $C_{12}H_{20}O$, which is a green, viscous liquid possessing but a slight odour and boiling at about 200° under 20 mm. pressure; it is readily soluble in alcohol or ether and neither combines with bromine nor yields an oxime; it is formed either by the condensation of 3 mols. of butane-$\alpha\gamma$-diol with elimination of $5H_2O$ or by the condensation of *n*-butaldehyde or methyl ethyl ketone. T. H. P.

$\alpha\beta\beta$-Trichloroethyl Ether. GIUSEPPE ODDO and EFISIO MAMELI (*Gazzetta*, 1903, 33, ii, 373—419).—*$\alpha\beta\beta$-Trichloroethyl ether*,

$CHCl_2 \cdot CHCl \cdot OEt$,

forms 80 per cent. of the product obtained by chlorinating $\alpha\beta$-dichloroethyl ether in a reflux apparatus with 1 mol. of chlorine at the temperature of boiling saturated salt solution; when purified by fractional distillation under atmospheric pressure, it boils at 170—175° and has a sp. gr. 1·3303 at 14°. When boiled for 250 hours, it loses hydrogen chloride, giving principally ethyl $\beta\beta$-dichlorovinyl ether, $CCl_2\!:\!CH \cdot OEt$ (Godefroy, Abstr., 1886, 606), which boils at 144—146°, and a *polymeride* of this, $(C_4H_6OCl_2)_2$, which boils at 187—192° under 30 mm. pressure and is unsaturated.

$\beta\beta$ Dichloro-$\alpha\beta$-dibromoethyl ether, $CCl_2Br \cdot CHBr \cdot OEt$, prepared by the addition of bromine to $\beta\beta$-dichlorovinyl ethyl ether, boils at 127—132° under 25—30 mm. pressure. $\alpha\beta\beta$-Trichloroethyl ether is not changed when heated in a sealed tube for several hours at 215°, but at 230—240° is resolved principally into dichloroacetaldehyde and ethyl chloride; the same products are formed, but in small quantity, when dry hydrogen chloride is passed through the trichloroether for 6 hours at 110°, and when $\alpha\beta\beta$-trichloroethyl ether is distilled with concentrated sulphuric acid the yield of dichloroacetaldehyde is 25 per cent. that of theory; this gives a better method of preparing the chlorinated aldehyde than that of Grimaux and Adam (*Bull. Soc. chim.*, 1880, [ii], 34, 29). Conversely, $\alpha\beta\beta$-trichloroethyl ether can be synthesised by passing hydrogen chloride into an alcoholic solution of dichloroacetaldehyde, the compound, $CHCl_2 \cdot CH(OH) \cdot OEt$, probably being formed as an intermediate product.

When boiled with water, $\alpha\beta\beta$-trichloroethyl ether gives a complex mixture which fractional distillation resolves into acetaldehyde, $\beta\beta$-dichloroacetaldehyde hydrate, the substance

$CHCl_2 \cdot CHO,2CHCl_2 \cdot CH(OH) \cdot OEt$;

dichloroacetal, $CHCl_2 \cdot CH(OEt)_2$; the ether,

$OEt \cdot CH(CHCl_2) \cdot O \cdot CH(CHCl_2) \cdot OEt$,

derived from the alcoholate of dichloroacetaldehyde, and the acetal, $OEt \cdot CH(CHCl_2) \cdot O \cdot CH(CHCl_2) \cdot O \cdot CH(CHCl_2) \cdot OEt$, formed from the condensation of 1 mol. of chloroacetaldehyde hydrate and 2 mols. of dichloroacetaldehyde alcoholate. The mechanism of the reaction is discussed. The following substances of those mentioned are new or hitherto have been described incorrectly.

Dichloroacetaldehyde hydrate, $CHCl_2 \cdot CH(OH)_2$, forms large, colourless, quadrangular plates, melts at 55—56°, and boils at 96·5—97·5°; Fritsch and Schumacher's dihydrate, $CHCl_2 \cdot CHO,2H_2O$ (Abstr., 1894,

i, 485), is really the *substance*, $CHCl_2 \cdot CHO,2CHCl_2 \cdot CH(OH) \cdot OEt$, which boils at 110—111° and is probably not a definite compound but a mixture of constant boiling point, as the molecular weight, determined by the cryoscopic method, has a value one-third of the calculated. On keeping, it decomposes giving dichloroacetaldehyde hydrate, dichloroacetal, and the solid melting at 82°, and with alcohol it forms dichloroacetaldehyde alcoholate, $CHCl_2 \cdot CH(OH) \cdot OEt$, which boils at 109·5—111° and has a sp. gr. 1·314 at 26°; Fritsch and Schumacher's "dichloroacetaldehyde alcoholate" was a mixture.

The *ether*, $[OEt \cdot CH(CHCl_2)]_2O$, boils at 183—188°; it was not obtained pure.

The *acetal*, $OEt \cdot CH(CHCl_2) \cdot O \cdot CH(CHCl_2) \cdot O \cdot CH(CHCl_2) \cdot OEt$, crystallises from light petroleum in long, white needles and melts at 82—84°.

The action of alkalis on $\alpha\beta\beta$-trichloroethyl ether gives complex products which are still being investigated; in no case is ethyl dichlorovinyl ether formed.

On boiling $\alpha\beta\beta$-trichloroethyl ether with alcohol, it gives dichloroacetal, $CHCl_2 \cdot CH(OEt)_2$; with methyl alcohol, *ββ-dichloro-αα-dimethoxyethane*, $CHCl_2 \cdot CH(OMe)_2$, boiling at 166—168°, is obtained, and *ββ-dichloro-α-methoxy-α-ethoxyethane*, which boils at 173—175°, being partly decomposed into ββ-dichloro-αα-dimethoxyethane and dichloroacetal.

By sodium methoxide in ethereal solution, αββ-trichloroethyl ether is converted into ethyl dichlorovinyl ether, and by boiling propyl alcohol, into *ββ-dichloro-αα-dipropoxyethane*, boiling at 212—214°, and *ββ-dichloro-α-ethoxy-α-propoxyethane*, which boils at 202—204°; both these substances, when heated with concentrated sulphuric acid, give dichloroacetaldehyde. W. A. D.

n-Propyl Ether and the Products of its Direct Chlorination. Giuseppe Oddo and Guido Cusmano (*Gazzetta*, 1903, 33, ii, 419—427).—Details are given for preparing *n*-propyl ether by the action of sulphuric acid on *n*-propyl alcohol, and of ferric chloride on the same substance. It boils at 89—91°, and on passing chlorine through it at the ordinary temperature until an increase of weight is obtained corresponding with two atoms of chlorine, a mixture of *dichloro-* and *trichloro-*n*-propyl ethers* is formed. The former, which boils at 80° under 15 mm. and at 176° under 762 mm. pressure, is perhaps identical with Brochet's compound (Abstr., 1896, i, 114); the latter boils at 133—138° under 2—3 mm. pressure, and is decomposed when distilled under atmospheric pressure. W. A. D.

Phosphoric Esters of Ethylene Glycol. Paul Carré (*Compt. rend.*, 1904, 138, 374—375).—When molecular proportions of phosphoric acid and ethylene glycol are heated for 10 hours at 140—145° under 15—18 mm. pressure, 89·9 per cent. of the phosphoric acid is esterified, the product consisting of 3·5 per cent. of the tri-ester, 42·4 per cent. of the di-ester, and 44 per cent. of the mono-ester; by increasing the quantity of glycol to two molecular proportions, the yield of the tri-ester can be raised to 14·5 per cent. The di- and tri-esters are converted into the mono-ester by hydrolysis with water, and as they present no differences in solubility to the mono-ester they have not been isolated. The mono-ester, *glycyl*

dihydrogen phosphate, $2PO(OH)_2\cdot O\cdot CH_2\cdot CH_2\cdot OH,H_2O$, is isolated by decomposing its lead salt with hydrogen sulphide. *Barium glycyl phosphate*, $PO(O_2Ba)\cdot O\cdot C_2H_5O,H_2O$, loses a molecular proportion of water at 180°. *Quinine glycyl phosphate*,

$$PO(OH)_2\cdot O\cdot C_2H_5O,(C_{20}H_{24}O_2N_2)_2,4H_2O,$$

and *quinine glycyl hydrogen phosphate*,

$$PO(OH)_2\cdot O\cdot C_2H_5O,(C_{20}H_{24}O_2N_2),2H_2O,$$

crystallise in thin needles, but effloresce at the ordinary temperature losing one molecular proportion of water. M. A. W.

Preparation of the Chlorides and Anhydrides of Organic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 146690).—Chlorosulphonic acid reacts with organic acids to form sulpho-derivatives; when, however, carboxylic acids or their salts are warmed with metallic chlorosulphonates, the chlorides of the organic acids are produced: $RCO_2Na + ClSO_3Na = RCOCl + Na_2SO_4$. Acid anhydrides are obtained when the proportion of organic acid is doubled. The chlorosulphonates are prepared by heating chlorosulphonic acid with the calculated quantity of the corresponding metallic chloride at 150°, moisture being excluded. The preparation of acetyl and benzoyl chlorides, and of acetic and benzoic anhydrides, is described. C. H. D.

Electrolysis of Fused Organic Salts. ERNST BERL (*Ber.*, 1904, 37, 325—331).—It is difficult to obtain satisfactory results on electrolysing fused organic salts, because nearly all begin to decompose in absence of a current at a temperature slightly above their melting points; moreover, they are such bad conductors that the heat produced by their resistance to a current intensifies this decomposition. When fused sodium acetate is electrolysed with a current of 0·2 ampere at 8 volts, a gaseous mixture consisting of 20·86 per cent. of carbon dioxide, 43·56 per cent. of hydrogen, and 25·92 per cent. of methane is obtained; it is shown that the hydrocarbon, which is here liberated at the cathode instead of at the anode, as in solution (compare Lassar-Cohn, Abstr., 1889, 1056), is produced by a secondary change, namely, the action of the metallic sodium on the fused salt, which gives rise also to sodium carbonate and carbon. Potassium acetate, under similar conditions, gives the same products, whilst potassium propionate gives 70·4 per cent. of hydrogen and 20·8 per cent. of ethane. Schall and Klien's observation (Abstr., 1889, i, 425) of the production of nitrobenzene from potassium *o*-nitrobenzoate is confirmed and shown to be due similarly to the action of metallic potassium on the fused salt. W. A. D.

Salts of Antimony with Organic Acids. II. EDUARD JORDIS and WILHELM MEYER (*Zeit. angew. Chem.*, 1904, 17, 169—175, 204—208, 236—239. Compare this vol., i, 216).—Antimony acetate, formed by heating antimony oxide (1 mol.) with acetic anhydride (5 mols.) until all is dissolved, is crystalline, and is unstable at the ordinary temperature. The solubility of antimony oxide in formic, acetic, chloroacetic, dichloroacetic, trichloroacetic, propionic, butyric, oxalic, malonic, succinic, maleic, fumaric, glycollic, lactic, tartaric,

citric, benzoic, salicylic, *p*-nitrosalicylic, and gallic acids respectively and in tannin has been examined. A. McK.

Chlorination by means of Sulphuryl Chloride. Alfred Wohl (D.R.-P. 146796).—Sulphuryl chloride may conveniently be employed as a chlorinating agent by carrying out the operation in a closed vessel under pressure. Air is pumped into the vessel at the commencement of the heating, and the evolved gases pass through a condenser, escaping by a valve under the desired constant pressure. Chloroacetic acid is thus prepared by heating acetic acid with sulphuryl chloride at 115—120° under 4—5 atmospheres' pressure. C. H. D.

Bromopivalic Acid [β-Bromo-αα-dimethylpropionic Acid] and its Derivatives. Edmond E. Blaise and L. Marcilly (*Bull. Soc. chim.*, 1904, [iii], 31, 155—160. Compare Reformatsky, Abstr., 1890, 1096).—When β-hydroxy-αα-dimethylpropionic acid (this vol., i, 219) (1 mol.) is treated with phosphorus pentabromide (2 mols.), there are formed *β-bromo-αα-dimethylpropionic acid* and *phospho-di-β-hydroxy-αα-dimethylpropionic acid.* The former is crystalline, melts at 40·5—41°, distils at 143—145° under 33 mm. pressure, and is very soluble in alcohol or ether. On exposure to air, the crystals liquefy and darken. When treated with potassium hydroxide, dissolved in water, the corresponding hydroxy-acid is reproduced. The *ethyl* ester, obtained either by esterifying the acid or by treating ethyl hydroxydimethylpropionate with phosphorus pentabromide, boils at 89—90° under 25 mm. pressure.

Phospho-di-β-oxy-αα-dimethylpropionic acid,

$$OH\cdot PO(O\cdot CH_2\cdot CMe_2\cdot CO_2H)_2,H_2O,$$

crystallises from ethyl acetate in white, cauliflower-like masses of slender needles, melts, when rapidly heated, at 110—120°, but when slowly heated or previously dehydrated, at 148°; the acid is not decomposed when warmed with sulphuric acid or with a 50 per cent. aqueous solution of potassium hydroxide, but is attacked by fused sodium nitrate, forming phosphoric acid. The *potassium* salt, $(C_{10}H_{16}O_8PK_3)_2,5H_2O$, prepared by neutralising the acid with potassium hydroxide, using phenolphthalein as indicator, forms colourless crystals. *Ethyl hydrogen phospho-di-oxydimethylpropionate*, $OH\cdot PO(O\cdot CH_2\cdot CMe_2\cdot CO_2Et)_2$, obtained by the action of phosphorus pentabromide on ethyl hydroxydimethylpropionate, is a colourless liquid, which cannot be distilled. There is also formed in this reaction a small quantity of an oily *substance*, which may be the normal ester, $PO(O\cdot CH_2\cdot CMe_2\cdot CO_2Et)_3$.

T. A. H.

Theory of Saponification. Julius Lewkowitsch (*Ber.*, 1904, 37, 884. Compare Abstr., 1903, i, 547; this vol., i, 6, 216).—Polemical: a reply to Balbiano. J. J. S.

Conversion of Paraffins into Alcohols and Fatty Acids during the Saponification of Spermaceti. G. Reale (*Chem. Zeit.*, 1904, 28, 242—243).—When spermaceti is saponified in the presence

of petroleum, the hydrocarbons of the petroleum are at the same time attacked by the alkali hydroxide with formation of an alcohol, the corresponding acid and hydrogen. Butane, for instance, is transformed into butyl alcohol, potassium butyrate, and hydrogen.

A. McK.

Biochemical Syntheses of Olein and some Esters. Henri Pottevin (*Compt. rend.*, 1904, 138, 378—380. Compare Abstr., 1903, ii, 494).—In addition to the mono-olein already described, triolein is prepared by the action of the pancreatic ferment on mixtures of the mono-olein and oleic acid at 36°; it is a neutral fat, solidifies at about 0°, and has a sp. gr. 0·915 at 15°. This esterifying action of the pancreatic ferment has also been extended to alcohols and acids other than glycerol and oleic acid; thus, under suitable conditions of concentration and temperature, methyl, ethyl, and *iso*amyl alcohols react with oleic acid; stearic acid with amyl alcohol; acetic, butyric, and propionic acids with amyl alcohol, provided the quantity of alcohol present is not greater than 100 grams to 8 grams of the acid. *d*- and *l*-Lactic acids and benzoic acid are not sensitive to the action of the ferment, in fact, the esterification of a mixture of oleic acid and amyl alcohol is retarded by 0·4 per cent. of lactic acid, whilst 0·8 per cent. stops it altogether.

iso*Amyl oleate* is a neutral, odourless liquid, which does not solidify at 0° and has a sp. gr. 0·897 at 15°. iso*Amyl stearate* is a neutral, white solid melting at 21°, is insoluble in water, soluble in ether, and can be obtained in the form of small, square, crystalline plates from a solution of warm alcohol.

M. A. W.

Action of Hydrogen Cyanide on Methyloldimethylacetaldehyde. Erhard Glaser (*Monatsh.*, 1904, 25, 46—54).—On treating methyloldimethylacetaldehyde with hydrogen cyanide and hydrolysing the impure cyanohydrin thus obtained with dilute hydrochloric acid, the main product consists of the *hydroxylactone*,

$$CMe_2<\begin{matrix}CH_2\text{—}O\\CH(OH)\end{matrix}>CO,$$

which solidifies to a drusy mass of prismatic needles melting at 55° and boiling at 115—117°; it is extremely hygroscopic and dissolves readily in water, ether, benzene, chloroform, alcohol, or carbon disulphide; of the corresponding acid, the *calcium* salt, $(C_6H_{11}O_4)_2Ca,3H_2O$, and the *silver* salt (with $8H_2O$) were prepared; the *acetyl* derivative of the lactone, $C_8H_{12}O_4$, is a colourless, almost odourless liquid boiling at 122—125° under 11 mm. pressure. Attempts to reduce the hydroxy-lactone to the corresponding lactone or to α-hydroxy-ββ-dimethylpropionic or ββ-dimethylpropionic acid were unsuccessful.

If, in preparing the lactone, the hydrochloric acid solution is left for 2 or 3 days in contact with the ethereal solution of the cyanohydrin, there remain, after removal of the ether, an oily liquid and white, acicular crystals, which do not contain nitrogen, melt at 156°, and are readily soluble in ether. On heating the oily liquid with hydrochloric acid, it yields a substance separating from ether in rhombic crystals melting at 182°.

T. H. P.

Alkyloxyalkylethylenic Acids and Hydrocarbons. CHARLES MOUREU (*Compt. rend.*, 1904, 138, 286—289. Compare next page).—The author has prepared the following acids by hydrolysis of the corresponding ester: *β-methoxy-β-amylacrylic acid*,

$$C_5H_{11}\cdot C(OMe){:}CH\cdot CO_2H,$$

melting at 54·5°, *β-ethoxy-β-amylacrylic acid*, $C_5H_{11}\cdot C(OEt){:}CH\cdot CO_2H$, melting at 74°, *β-propoxy-β-amylacrylic acid*, $C_5H_{11}\cdot C(OPr^{\alpha}){:}CH\cdot CO_2H$, melting at 58°, *β-methoxy-β-hexylacrylic acid*, $C_6H_{13}\cdot C(OMe){:}CH\cdot CO_2H$, melting at 55·5°, *β-methoxycinnamic acid*, $OMe\cdot CPh{:}CH\cdot CO_2H$, decomposing at about 180°, and *β-ethoxycinnamic acid*,

$$OEt\cdot CPh{:}CH\cdot CO_2H,$$

which decomposes at about 160°. These acids are not hydrolysed by ferric chloride, and therefore give no coloration with that reagent; they are readily hydrolysed by warm dilute sulphuric acid with the formation of the corresponding ketone, according to the equation $C_5H_{11}\cdot C(OMe){:}CH\cdot CO_2H + H_2O = C_5H_{11}\cdot CO\cdot CH_3 + MeOH + H_2O + CO_2$; and on being heated, lose carbon dioxide and form the corresponding alkyloxyalkylethylene, of which the following were prepared: *ββ-methoxy-Δ^α-heptylene*, $C_5H_{11}\cdot C(OMe){:}CH_2$, boiling at 145·5°, *ββ-ethoxy-Δ^α-heptylene*, $C_5H_{11}\cdot C(OEt){:}CH_2$, boiling at 161—161·5°, *β-propoxy-Δ^α-heptylene*, $C_5H_{11}\cdot C(OPr^{\alpha}){:}CH_2$, boiling at 181—182°, *β-methoxy-Δ^α-octylene*, $C_6H_{13}\cdot C(OMe){:}CH_2$, boiling at 166—168°, *β-methoxy-β-phenylethylene*, $OMe\cdot CPh{:}CH_2$, boiling at 197°, and β-ethoxy-β-phenylethylene, $OEt\cdot CPh{:}CH_2$, boiling at 209—210°, previously prepared by Claisen (compare Abstr., 1896, i, 464). These compounds are readily hydrolysed by dilute sulphuric acid, yielding the corresponding ketone, thus: $C_6H_{13}\cdot C(OMe){:}CH_2 + H_2O = CH_3\cdot OH + C_6H_{13}\cdot CO\cdot CH_3$. Attempts to prepare α-alkyloxy-β-alkylethylenic compounds of the type $CHR{:}CH(OR')$ by condensing the corresponding alkylacetylene, $CR{:}CH$, with alcohol in the presence of sodium were unsuccessful owing to the transformation of the acetylene into its symmetrical isomeride by the action of the alkali (compare Faworsky, Abstr., 1888, 798), thus, Δ^{α}-heptinene, $C_5H_{11}\cdot C{:}CH$, was converted into Δ^{β}-heptinene, $C_4H_9\cdot C{:}CMe$. Phenylacetylene, however, gives normal condensation products with alcohols in the presence of sodium, and the following compounds were prepared: *α-methoxystyrene*, $CPhH{:}CH\cdot OMe$, boiling at 210—213°, *α-ethoxystyrene*, $CPhH{:}CH\cdot OEt$, boiling at 225—226°, *α-propoxystyrene*, $CPhH{:}CH\cdot OPr^{\alpha}$, boiling at 238—241°, α-iso*butoxystyrene*, $CPhH{:}CH\cdot OC_4H_9$, boiling at 248—251°. These compounds are hydrolysed by dilute sulphuric acid with the formation of phenylacetaldehyde, according to the equation:

$$CPhH{:}CH\cdot O\cdot C_4H_9 + H_2O = Ph\cdot CH_2\cdot CHO + C_4H_9\cdot OH.$$

M. A. W.

β-Aldehydo-esters. EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 160—170).—Previous attempts to prepare β-aldehydo-acids have given rise to the production of the isomeric unsaturated secondary alcohols (Wislicenus, Abstr., 1888, 129, and von Pechmann, Abstr., 1892, 816). When ethyl β-hydroxy-αα-dimethylpropionate (this vol., i, 219) is oxidised with chromic acid in the absence of a solvent, small quantities of a substance giving the

reactions of an aldehyde are produced, but most of the original ester is recovered unchanged. When the oxidation is effected in acetic acid solution at 0°, the principal products are ethyl hydrogen dimethylmalonate, and the *ester*, $CO_2Et\cdot CMe_2\cdot CO_2\cdot CH_2\cdot CMe_2\cdot CO_2Et$, formed by the interaction of this with ethyl hydroxydimethylpropionate, which boils at 156—157° under 18 mm. pressure, and on hydrolysis furnishes hydroxydimethylpropionic and dimethylmalonic acids. There is also produced, however, a small quantity of *ethyl formyl*iso*butyrate*, $CHO\cdot CMe_2\cdot CO_2Et$, which is best isolated as its sodium bisulphite compound. This ester is a colourless, mobile oil with a pronounced aldehydic odour; it boils at 65—66° under 20 mm. pressure, has a sp. gr. 0·9834 at 20°/4° and gives the usual aldehyde reactions, but does not give a coloration with ferric chloride. The *semicarbazone* crystallises in needles and melts at 161—162°.

When treated with phenylhydrazine, *ethyl formyl*iso*butyrate* is converted into 1-*phenyl*-4 : 4-*dimethyl*-5-*pyrazolone*, $NPh<\begin{matrix}N{=}CH\\ CO\cdot CMe_2\end{matrix}$, which crystallises in needles, melts at 51°, and is very soluble in ether.

Ethyl formyl*iso*butyrate, when hydrolysed by ebullition with dilute sulphuric acid, furnishes *iso*butaldehyde (the *semicarbazone* forms large leaflets melting at 126—127°) and carbon dioxide. When hydrolysed with baryta water, there are formed in addition to *iso*butaldehyde, ethyl *iso*butyrate and formic acid.

The β-aldehydo-esters resemble the β-ketonic esters, but are less stable than these compounds, owing to the greater reactivity of the formyl radicle as compared with its higher homologues. T. A. H.

Ethyl γ-Chloroacetoacetate. Robert Lespieau (*Compt. rend.*, 1904, 38, 421—423).—Ethyl γ-chloroacetoacetate is formed by carefully oxidising the ethyl γ-chloro-β-hydroxypropionate with potassium dichromate and sulphuric acid. The ketonic ester may be isolated from the reaction product by means of its insoluble copper derivative, which separates on shaking the oxidation product with aqueous copper acetate. This copper derivative dissolves in hot benzene, and is deposited from the cold medium in green crystals which melt at 168°. Ethyl γ-chloroacetoacetate forms a colourless liquid which boils at 105° under 11 mm. pressure, with considerable decomposition at 205° under the ordinary pressure, and has a sp. gr. 1·23 at 0°. The ester, when added to solutions of ferric salts, develops a deep reddish-violet coloration. S. S.

Condensation of Acetylenic Esters with Alcohols. II. Charles Moureu (*Compt. rend.*, 1904, 138, 206—209. Compare Abstr., 1903, i, 698).—The condensation of the acetylenic esters with alcohols to form the corresponding saturated acetal derivatives is a general reaction. *Ethyl αα-diethoxyphenylpropionate*,

$$CPh(OEt)_2\cdot CH_2\cdot CO_2Et,$$

prepared from ethyl phenylpropiolate and ethyl alcohol, boils at 153° (corr.) under 13 mm. pressure, and on saponification yields the corre-

sponding acid in the form of white crystals melting at 68° with evolution of gas; both the acid and its ester are rapidly coloured red by an alcoholic solution of ferric chloride; this is due to the formation of benzoylacetic acid by the hydrolytic action of the ferric chloride.

When esters of the above type are heated at about 175°, they readily lose one molecular proportion of alcohol and yield the corresponding ethylenic compound in theoretical quantity; the following compounds were thus prepared: *methyl β-methoxy-β-amylacrylate*,

$$C_5H_{11}\cdot C(OMe)\colon CH\cdot CO_2Me,$$

boiling at 232—233° (corr.); *ethyl β-ethoxy-β-amylacrylate*,

$$C_5H_{11}\cdot C(OEt)\colon CH\cdot CO_2Et,$$

boiling at 253—253·5° (corr.); *propyl β-propoxy-β-amylacrylate*,

$$C_5H_{11}\cdot C(OPr^{\alpha})\colon CH\cdot CO_2Pr^{\alpha},$$

boiling at 279—280° (corr.); *methyl β-methoxy-β-hexylacrylate*,

$$C_6H_{13}\cdot C(OMe)\colon CH\cdot CO_2Me,$$

boiling at 245—248°; *methyl β-methoxycinnamate*,

$$OMe\cdot CPh\colon CH\cdot CO_2Me,$$

boiling at 154—155° (corr.) under 14 mm. pressure, and *ethyl β-ethoxycinnamate*, $OEt\cdot CPh\colon CH\cdot CO_2Et$, boiling at 167—168° (corr.) under 16 mm. pressure, previously prepared by Claisen (compare Abstr., 1896, i, 463).

With the exception of the last, these compounds are not readily hydrolysed, and thus give only a feeble coloration with ferric chloride. The four esters of the aliphatic series are readily hydrolysed by warm sulphuric acid yielding the ester of the corresponding β-ketonic acid, thus methyl β-methoxy-β-amylacrylate gives methyl hexoylacetate,

$$C_5H_{11}\cdot C(OMe)\colon CH\cdot CO_2Me + H_2O = MeOH + C_5H_{11}\cdot CO\cdot CH_2\cdot CO_2Me.$$

The two esters of the aromatic series give acetophenone on hydrolysis according to the equation: $CPh(OMe)\colon CH\cdot CO_2Me + 2H_2O = 2MeOH + C_6H_5\cdot CO\cdot CH_3 + CO_2$. M. A. W.

Baeyer's Tension Theory. ARNOLD F. HOLLEMAN and GERARDUS L. VOERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 410—412). —Since Baeyer's Tension theory is based on qualitative observations only, the authors have considered it from a quantitative standpoint by investigating the relative stability of the anhydrides of saturated dibasic acids with respect to water. The velocity with which those anhydrides are converted into their corresponding acids may be taken as a measure of the tension in the ring. Succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic anhydrides were examined, and the velocity of their conversion into acids was measured by the electric conductivity of the solution, the assumption being made that the solution of the anhydride is a non-conductor. As the concentration of the acid, after complete conversion of the anhydride, did not exceed $N/23$ in the velocity measurements, the quantity of water may be taken as constant, and the conversion is unimolecular.

Succinic and glutaric anhydrides only gave satisfactory constants at 25°; the figures show that the 5-membered ring is more stable than the 6-membered ring. Accurate measurement was not found to be possible in the case of the higher anhydrides, owing to their sparing solubility in water. Moreover, boiling point determinations of the

solutions of the higher anhydrides in acetone show that they are polymerised, whilst succinic and glutaric anhydrides give normal values.

A. McK.

α-Substituted β-Methyladipic Acids. Marcel Desfontaines (*Compt. rend.*, 1904, 138, 209—211).—The author has prepared the following esters of α-substituted *cyclo*pentanonecarboxylates by Dieckmann's method (compare Abstr., 1894, i, 173) from the esters of β-methyl*cyclo*pentanonecarboxylate, by the action of alkyl iodides in the presence of sodium wire in anhydrous ether or powdered sodium in toluene: *methyl* 1 : 5-*dimethyl*-2-cyclo*pentanone*-1-*carboxylate*, which boils at 105—106° under 15 mm. pressure and has a sp. gr. 1·065 at 0° and n_D 1·450 at 20°; *ethyl* 1 : 5-*dimethyl*-2-cyclo*pentanone*-1-*carboxylate*, which boils at 112—113° under 15 mm. pressure and has a sp. gr. 1·030 and n_D 1·444 at 19°; *methyl* 5-*methyl*-1-*allyl*cyclo*pentanone*-1-*carboxylate*, which boils at 114—115° under 15 mm. pressure; ethyl 5-methyl-1-allyl-2-*cyclo*pentanone-1-carboxylate, which boils at 139—141° under 18 mm. pressure (compare Haller and Desfontaines, Abstr., 1903, i, 628); *methyl* 5-*methyl*-1-*ethyl*-2-cyclo*pentanone*-1-*carboxylate*, which boils at 108—110° under 15 mm. pressure and has a sp. gr. 1·073 and n_D 1·456 at 15°; *methyl* 5-*methyl*-1-*propyl*-2-cyclo*pentanone*-1-*carboxylate*, which boils at 138—140° under 22 mm. pressure; *ethyl* 5-*methyl*-1-*ethyl*-2-cyclo*pentanone*-1-*carboxylate*, which boils at 119—120° under 18 mm. pressure; *ethyl* 5-*methyl*-1-*propyl*-2-cyclo*pentanone*-1-*carboxylate*, which boils at 136—137° under 17 mm. pressure; and *ethyl* 5-*methyl*-1-iso*butyl*-2-cyclo*pentanone*-1-*carboxylate*, which boils at 188—190° under 18 mm. pressure.

All these esters are readily saponified by alcoholic potassium hydroxide, yielding the corresponding substituted adipic acid, according to the equation:

$$\begin{matrix} CH_2\text{——}CO \\ | \\ CH_2\cdot CHMe \end{matrix}\!\!>\!CR'\cdot CO_2R \longrightarrow CO_2R\cdot CH_2\cdot CH_2\cdot CHMe\cdot CHR'\cdot CO_2H,$$

and the following new compounds were thus prepared: *αβ-dimethyladipic acid*, which boils at 214—216° under 18 mm. pressure, melts at 80°, and forms a dianilide melting at 158°; *β-methyl-α-ethyladipic acid*, which melts at 97—98°; *β-methyl-α-propyladipic acid*, which melts at 110°; and *β-methyl-α-allyladipic acid*, which melts at 104°.

M. A. W.

Condensation of *iso*Butyrylformaldol with Malonic Acid. Arthur Silberstein (*Monatsh.*, 1904, 25, 12—20).—The condensation of *iso*butyrylformaldol with malonic acid in presence of alcoholic ammonia yields: (1) the *lactone* of *γ-dimethylmethylolcrotonic acid*, $CMe_2<\begin{matrix}CH_2-O\\CH:CH\end{matrix}>CO$, which separates from alcohol in needles melting at 177° and is soluble in ether, carbon disulphide, or benzene; in freezing benzene, it has double the normal molecular weight; when boiled with barium hydroxide solution, it yields the *barium* salt of the corresponding *hydroxy-acid*, $(C_7H_{11}O_3)_2Ba$; its *dibromide*, $C_7H_{10}O_2Br_2$, separates from benzene in crystals melting and decomposing (?) at 152°.

(2) The *ammonium* salt of the *lactonic acid* of *aγ-dihydroxy-ββ-dimethylpropylmalonic acid*, $CMe_2<\begin{matrix}CH_2\text{—}O\cdot CO\\ CH(OH)\cdot CH\cdot CO_2H\end{matrix}$; the *acid* crystallises from water in star-shaped aggregates of shining needles melting at 82° and is soluble in ether; its *calcium* salt was prepared and analysed; oxidation of the acid with alkaline potassium permanganate solution yields malonic and dimethylmalonic acids.

The first product of the condensation of *iso*butyrylformaldol and malonic acid by means of alcoholic ammonia is the ammonium salt (2), which then loses ammonia, carbon dioxide, and water yielding the lactone (1). T. H. P.

Formaldehyde in Atmospheric Air. H. Henriet (*Compt. rend.* 1904, **138**, 203—205. Compare Abstr., 1902, i, 714; 1903, i, 600).—On distilling the liquid obtained by evaporating to 200 c.c. 30 to 40 litres of condensed atmospheric moisture, the distillate contains in addition to formic acid an aldehyde which reduces Nessler's reagent, ammoniacal silver nitrate, and Fehling's solution, and gives a reddish-violet coloration with a solution of magenta decolorised by sulphurous acid. This aldehyde is identified with formaldehyde by the following specific reactions: (1) Lebbin's reaction, the formation of a red coloration on boiling the aldehydic solution with an alkaline solution of resorcinol. (2) Farnsteiner's reaction, the development of a rich violet colour with a dilute solution of peptone, sulphuric acid, and ferric chloride; this reaction, which is a very delicate test for formaldehyde, is also given by the liquid obtained by bubbling filtered air through distilled water. (3) The formation of hydrogen cyanide by distilling with sulphuric acid the product of the action of hydroxylamine hydrochloride on an alkaline solution of the liquid. (4). The formation of the blue colour of tetramethyldiaminobenzhydrol (Michler's hydrol), by oxidising the product obtained by boiling the aldehydic liquid with dimethylaniline and sulphuric acid.

The quantity of formaldehyde in the air varies from 1 to 5 parts per 100,000, and is proportional to the temperature. M. A. W.

Oxidation of Formaldehyde by Peroxides. Hans Geisow (*Ber.*, 1904, **37**, 515—520).—When formaldehyde is oxidised by hydrogen peroxide in neutral or acid solution, hydrogen is evolved, but no formic acid could be detected. The action proceeds thus: $CH_2O + H_2O_2 = CO_2 + H_2O + H_2$. In order to establish whether the hydrogen evolved had its origin from the formaldehyde used, experiments were made with barium peroxide and formaldehyde, when it was found that hydrogen was also evolved and that the barium peroxide was converted into carbonate. When the experiment was conducted with a dilute solution of formaldehyde and the temperature kept below the boiling point of water, no formate was obtained, but only carbonate.

The action of manganese peroxide and lead peroxide respectively

on formaldehyde led to the formation of the corresponding formates; neither carbon dioxide nor carbonate could be detected in either case.

A. McK.

Preparation of Acetone. L. WENGHÖFFER (D.R.-P. 144328).—A metallic acetate, in the form of a solution or in a pasty condition, is gradually introduced into a heated vessel. The moist mass is so rapidly decomposed that acetone and water-vapour pass off together, and local charring is avoided.

C. H. D.

Alkyl Allyl Ketones. EDMOND E. BLAISE (*Compt. rend.*, 1904, 138, 284—286).—With the view of extending his investigation on the acid nature of the hydrogen atoms of a methylene group situated between a carbonyl radicle and an ethylenic carbon atom (compare Abstr., 1903, i, 400, 549), the author has prepared a series of alkyl allyl ketones of the type $CH_2:CH\cdot CH_2\cdot COR$ by the condensation of allyl iodide with a fatty nitrile in benzene solution in the presence of zinc at a temperature of 0°, and the subsequent decomposition of the initial additive product by dilute sulphuric acid, according to the following equations: $CH_2:CH\cdot CH_2I + RCN + Zn = CH_2:CH\cdot CH_2\cdot CR:N\cdot ZnI$; $2CH_2:CH\cdot CH_2\cdot CR:N\cdot ZnI + 4H_2O = 2CH_2:CH\cdot CH_2\cdot COR + 2NH_3 + ZnOH + ZnI_2$. The ketones are colourless, mobile liquids, boiling without alteration under atmospheric pressure, and there is a difference of about 20° between the boiling points of two consecutive homologues; they have agreeable odours, readily form semicarbazones and liquid oximes which boil in a vacuum without alteration. Owing to their unsaturated character, they are readily oxidised by permanganate solution in the cold, and unite directly with the halogen acids with development of heat; the saturated brominated ketones obtained by the union of the alkyl allyl ketone with hydrogen bromide are very unstable, although they can be distilled in a vacuum without undergoing decomposition. The bromine in these compounds is in the β-position; on boiling with an alkali solution or even with water only, they lose hydrogen bromide, yielding the propenyl ketone isomeric with the original: $CH_2:CH\cdot CH_2\cdot COR \rightarrow CH_3\cdot CHBr\cdot CH_2\cdot COR \rightarrow CH_3\cdot CH:CH\cdot COR$. These propenyl ketones, also formed in small quantity in the preparation of the allyl ketones, boil about 10° lower than the isomeric allyl compound and readily form semicarbazones.

M. A. W.

Action of Titanium Tetrachloride on 1:3-Diketones. WALTHER DILTHEY (*Ber.*, 1904, 37, 588—592).—The products described by Rosenheim, Loewenstamm and Singer (Abstr., 1903, i, 603) are similarly constituted to the silicon derivatives previously prepared by the author (*ibid.*, 405, 591, and this vol., i, 132). The compound described as $TiCl_3\cdot CHAc_2,Et_2O$ is really $TiCl_2(CHAc_2)_2$, and may also be obtained from chloroform solutions. It may be crystallised from a small amount of glacial acetic acid, and appears to be termolecular. It forms a *compound* with ferric chloride, having the composition $TiFeCl_4(CHAc_2)_3$, and crystallising in reddish-yellow needles. The

platinichloride, $[Ti(CHAc_2)_3]_2PtCl_6$, crystallises in brownish-yellow prisms.

The compound described as $CO_2Et\cdot CAc\colon TiCl_2,Et_2O$ is really

$TiCl_2(CHAc\cdot CO_2Et)_2$. J. J. S.

Action of Dilute Sulphuric Acid on Butyronepinacone. KARL ZUMPFE (*Monatsh.*, 1904, 25, 124—134).—On heating butyronepinacone with 20 per cent. sulphuric acid in a sealed tube for 7 hours at 150° and then for 5 hours at 170—180°, a mixture is formed which contains principally the two following products:

(1) A *hydrocarbon*, $C_{14}H_{26}$, which is a colourless, oily liquid with a faint aromatic odour, and boils at 216—218° under the ordinary pressure, and at 98—100° under 13 mm. pressure; it is readily soluble in alcohol or ether, and yields a *dibromide*, $C_{14}H_{26}Br_2$, separating from carbon disulphide in scales melting at 83°; on oxidation with chromic acid, it gives acetic, propionic, and butyric acids.

(2) An *oxide*, $C_{14}H_{28}O$, which is a yellow, oily liquid with an empyreumatic smell and a bitter taste; it boils at 243—244° under the ordinary pressure, and at 122—124° under 13 mm., and on oxidation with chromic acid or permanganate yields only a trace of fatty acids; it does not give an oxime, acetyl derivative, or phenylhydrazone, and does not react with zinc ethyl or with water or aqueous alcohol in a sealed tube, and hence is probably a 1 : 4- or 1 : 5-oxide.

With boric acid also, butyronepinacone yields a mixture of the above hydrocarbon and oxide. T. H. P.

New Bases derived from Sugars. II. E. ROUX (*Ann. Chim. Phys.*, 1904, [viii], 1, 160—185).—The preparation, properties, and derivatives of arabinamine and of xylamine described in this paper have already been published (compare Abstr., 1903, i, 463). Arabinamine hydriodide melts without decomposition at 190—191°, and the picrate decomposes at 144—145°. Xylamine hydriodide melts without alteration at 206°, and has $[\alpha]_D - 12\cdot 50°$; the hydrochloride crystallises in deliquescent, prismatic needles, and is soluble in ethyl or methyl alcohol. M. A. W.

Mannamine, a New Base Derived from Mannose. E. ROUX (*Compt. rend.*, 1904, 138, 503—505. Compare Maquenne and Roux, Abstr., 1901, i, 372; 1902, i, 266, 696; 1903, i, 73, 463).—Mannamine, prepared by reducing mannoseoxime, is identical with the base formed together with glucamine when *iso*glucosamine is reduced by sodium amalgam (compare Maquenne, this vol., i, 18), and forms a partially crystalline mass very soluble in water or alcohol, which melts at about 139°, has a caustic but sweet taste, has $[\alpha]_D - 2°$ in 10 per cent. aqueous solution, and shows no multirotation. It forms a precipitate with nickel sulphate, and gives a white, amorphous product with mercuric chloride, insoluble in excess of the base. The *oxalate*, $(C_6H_{15}O_5N)_2,C_2O_4H_2$, forms brilliant, lozenge-shaped plates, melts at 186°, has $[\alpha]_D + 4\cdot 25°$ in 10 per cent. aqueous solution, is very soluble in water, but insoluble in alcohol, and loses 1 mol. of water on being heated for some time just above its melting point, forming *dimann-*

oxamide, $C_2O_2(NH\cdot C_6H_{13}O_5)_2$, which crystallises in thin, hexagonal plates melting at 218—219°, and is soluble in alcohol or water.

The *sulphate* and *hydrochloride* are crystalline and soluble in water, but insoluble in alcohol. The *platinichloride* crystallises in yellow, prismatic needles, and is slightly soluble in alcohol.

Mannaminecarbamide, $C_6H_{13}O_5\cdot NH\cdot CO\cdot NH_2$, prepared from potassium cyanate and mannamine sulphate, crystallises in tufts of slender, prismatic needles, melts at 97—98°, is readily soluble in water, but less so in alcohol. The *phenylcarbamide*, $C_6H_{13}O_5\cdot NH\cdot CO\cdot NHPh$, produced by the action of phenylcarbamide on mannamine in pyridine solution, crystallises in elongated, trapezoidal plates, which melt at 202° and are slightly soluble in alcohol or water.

Acetylacetonemannamine, $CH_2Ac\cdot CMe{:}N\cdot C_6H_{13}O_5$, obtained by the action of boiling acetylacetone on mannamine, forms thin, long needles, melts at 172°, is readily soluble in water or alcohol, and rapidly hydrolysed by dilute acids.

Benzylidenemannamine, $C_6H_{13}O_5\cdot N{:}CHPh$, produced by the condensation of benzaldehyde and mannamine, forms small crystals, decomposes at 183°, is slightly soluble in alcohol, and readily decomposed by cold water.

2-*Thiol*-5-*butyltetroloxazoline*,

$$\begin{array}{l}\mathrm{N\cdot CH_2} \\ \| \\ \mathrm{SH\cdot C\text{---}O}\end{array}\!\!>\mathrm{CH\cdot[CH\cdot OH]_3\cdot CH_2\cdot OH},$$

prepared by the action of carbon disulphide on mannamine, forms small, prismatic crystals, melts at 216°, is soluble in boiling water, slightly so in alcohol, and gives a crystalline derivative with silver nitrate. M. A. W.

Phenomena of Rotation of Lactose. HEINRICH TREY (*Zeit. physikal. Chem.*, 1903, 46, 620—719. Compare Abstr., 1896, ii, 139; 1897, ii, 299; also Hudson, Abstr., 1903, ii, 623).—The decrease in the rotation of lactose hydrate and the increase in that of lactose anhydride are changes which follow the same course as a reaction of the first order, and are represented by the formula $C = 1/t.\log A/(A - x)$. The velocity of the change of rotation for the hydrate is ten times greater at 25° than at 0°, for the anhydride eight times greater. Addition of methyl or ethyl alcohol retards both changes, and the retardation is nearly proportional to the amount of alcohol added. A similar remark applies to aqueous acetone solutions of lactose hydrate and anhydride. Both the decrease of rotation of lactose hydrate and the increase of rotation of lactose anhydride are accelerated by acids, and experiments at 0° have shown that the acceleration produced by an acid depends on its affinity constant. Sodium hydroxide and ammonia, when present in fair quantity, give at once the same rotation value in both hydrate and anhydride solutions, and this is followed by a slow decrease in both cases. In very dilute solutions, sodium hydroxide and ammonia do not at once produce the same rotation value, but accelerate the change of rotation of the hydrate and of the anhydride as indicated above in the case of acids. This accelerating effect is intensified by the addition of alcohol. Sodium carbonate and triammonium phosphate in $N/10$ solution also produce immediately

the constant rotation value of lactose hydrate. The effect of many other substances has been tested, for example, sodium hydrogen carbonate, borax, sodium tungstate, ammonium molybdate, carbamide, and neutral salts, such as barium chloride, magnesium sulphate, potassium iodide, and ammonium chloride. These substances accelerate the change of rotation both of the hydrate and of the anhydride. Sodium chloride is without effect.

The author attributes the changes of rotation described above to changes of configuration that take place gradually in solution.

J. C. P.

The Inversion of Sugar. LÉON LINDET (*Compt. rend.*, 1904, 138, 508—510).—The author has measured the electrolytic conductivity of 10 per cent. aqueous solutions of sugars which have been boiled for 4 hours, and finds that if the conductivity of distilled water is taken as unity, that of sucrose is 1·3, that of lævulose 3·7, and that of dextrose 5·1; the conductivity of sucrose is increased by the addition of 1/3000 of inverted sugar, and the different commercial raffinoses have a conductivity varying with the amount of dextrose they contain (compare Prinsen Geerligs, Abstr., 1899, i, 101; Kullgren, Abstr., 1901, ii, 149; 1902, ii, 647). Raýman and Šulc (compare Abstr., 1896, i, 459; 1897, ii, 136; 1898, i, 348; 1899, i, 102) have shown that sucrose is not inverted when heated with water in glass vessels, whilst in some metallic vessels the inversion proceeds rapidly; the author shows that the retarding influence of glass is to be attributed to the extraction by the water of alkali silicates, which neutralise the acid produced during the inversion and so check the process. The effect of metals in the form of powder or turnings on the inversion of sugar has also been examined, and it is found that copper, lead, tin, and bismuth are very active in this respect; aluminium and antimony are less so, whilst nickel, chromium, arsenic, gold, platinum, silver, and mercury are indifferent, and cobalt, iron, zinc, cadmium, and magnesium have a retarding influence. It is suggested that the hydroxide of the metal is formed by the action of the air and water, and this has an accelerating or retarding effect according as it is of an acidic or basic character, whilst those metals which are inert are also those which do not yield hydroxides under the conditions of the experiment.

M. A. W.

A Labile Nitrate of Cellulose. EDMUND KNECHT (*Ber.*, 1904, 37, 549—552).—When cellulose is soaked in nitric acid of sp. gr. 1·415, it takes up 36 per cent. of HNO_3, forming a compound $C_6H_{10}O_5,HNO_3$ (this requires 37·2 per cent. HNO_3), which is decomposed by water. The excess of acid cannot be removed satisfactorily by washing, but is got rid of by exposure in a desiccator over freshly burnt lime. The product obtained by the action of water contains 4 per cent. more water than normal cellulose and is probably a hydrate. Heating in a vacuum at 100° causes the liberation of nitrous fumes, and leaves a product, insoluble in sodium hydroxide and capable of reducing Fehling's solution, which appears to be identical with Cross and Bevan's oxycellulose. The process is closely

analogous to that involved in mercerisation, in which the cellulose forms an additive compound, $C_6H_{10}O_5,Na_2O$, in which (on washing with water) the soda is replaced by water forming a hydrate; after treatment with nitric acid and water, the cellulose fibres were found to have shrunk 13 per cent. and to have increased greatly in tensile strength.

T. M. L.

Formation and Saccharification of Reverted Starch. Léon Maquenne (*Compt. rend.*, 1904, 138, 213—214. Compare Abstr., 1903, i, 679; this vol., i, 17, 227).—In the experiments hitherto made on the reversion (transformation) of starch paste, fairly concentrated solutions of the paste have been used; it is now found that the extent of the reversion, as measured by the amount of amylocellulose formed, increases with the concentration of the starch paste, at first rapidly, but afterwards more slowly. The amylocellulose formed by the reversion of starch paste is partly rendered soluble by amylase if the saccharification is conducted at a sufficiently high temperature, but it never becomes entirely soluble, even after being heated anew to 130°. It is probable that amylocellulose is not a definite compound, but a mixture of several different condensation products which have the property in common of not being coloured by iodine, and the distinctive characteristics of offering specific resistances to the solvent action of amylase. M. A. W.

Nature of Raw Starch. Léon Maquenne (*Compt. rend.*, 1904, 138, 375—377. Compare Abstr., 1903, i, 675; this vol., i, 17). —The paste freshly prepared from raw starch is rendered completely soluble by amylase or by mineral acids; only 2·8 per cent. of the raw starch grains becomes soluble under similar treatment, whilst 94·8 per cent. becomes soluble if the grains have been previously pulverised, thus, as Brown and Héron have shown, the effect of mechanically destroying the protecting envelope of the grains is almost the same as that produced by converting it into a jelly. From a chemical point of view, therefore, the starch grain possesses the same composition as starch paste which has been prepared some time, that is, it is *reverted starch*, a mixture of amylocelluloses in various states of condensation. It is because these amylocelluloses redissolve at a high temperature that they are not present in freshly prepared starch paste, and because they are formed from pure starch in the cold that they are present in raw starch grains and reverted starch. M. A. W.

Composition of Potato-starch. Auguste Fernbach (*Compt. rend.*, 1904, 138, 428—430).—When potato-starch is levigated, two kinds of granules, the heavy and the light, are obtained. Both of these contain phosphorus, and analysis shows that the light granules contain a greater percentage of that element than the heavy grains. In six samples examined, the heavy granules contained 138—178 mg. P_2O_5, and the lighter granules 158—226 mg. P_2O_5 per 100 grams.

S. S.

Pure Glycogen. MADAME Z. GATIN-GRUZEWSKA (*Pflüger's Archiv*, 1903, 100, 634—635).—Pure glycogen, obtained by Pflüger's method and quite free from nitrogen, when precipitated by alcohol from an aqueous solution, comes down in the shape of clumps and rods, with forms intermediate between them. In some cases, the rods are quite long. This character is recommended as a criterion of the purity of glycogen. W. D. H.

Electrolytic Preparation of Fatty Amines. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148054).—The products of condensation of aldehydes with ammonia may be conveniently reduced by electrolysis in neutral or ammoniacal solution. Thus a solution of hexamethylenetetramine and sodium sulphate may be electrolysed between lead electrodes, employing a current-density of 3 amperes per sq. dm., and a potential difference of 3·5 volts, sulphuric acid being added from time to time in the neighbourhood of the cathode to maintain neutrality. In place of the condensation products, a mixture of the aldehyde with ammonia or ammonium salts may be electrolysed directly. C. H. D.

[Electrolytic] Preparation of Nitro- and Amino-compounds. MORITZ LILIENFELD (D.R.-P. 147943).—In the removal of the carboxyl group from fatty or aromatic carboxylic acids by electrolysis, the copper salts may advantageously be employed in place of the alkali salts. The evolution of gas at the electrodes is thus avoided, as well as the formation of an alkali hydroxide, which may give rise to secondary reactions. The conductivity of the copper salts is also greater than that of the alkali salts, and the end of the reaction is easily determined by the disappearance of the blue colour. Thus a solution of copper glycine, electrolysed with a current-density of 0·1 ampere per 1000 sq. mm., and a tension of 1·75 volts, yields ethylenediamine, $Cu(CO_2 \cdot CH_2 \cdot NH_2)_2 = Cu + 2CO_2 + C_2H_4(NH_2)_2$. The preparation of benzidine from copper *p*-aminobenzoate, and that of *p*-dinitrodiphenyl from copper *p*-nitrobenzoate, are also described. When nitro-acids are employed, the electrolysis may be continued until the nitro-group has been reduced to the amino-group. The salts of other heavy metals may be employed in place of copper salts, but with less advantage. C. H. D.

Preparation of Aminoaldehydes. CARL D. HARRIES and PAUL REICHARD (*Ber.*, 1904, 37, 612—615).—An aqueous solution of allylamine hydrochloride is readily oxidised by ozone to aminoacetaldehyde hydrochloride, hydrogen peroxide being formed at the same time.

The *platinichloride*, $[CHO \cdot CH_2 \cdot NH_2]_2,H_2PtCl_6$, crystallises in pale yellow plates melting and decomposing at 185°, and is quite different from the platinichloride described by E. Fischer (Abstr., 1893, i, 187, 300). Fischer's aminoacetaldehyde also yields a platinichloride free from alcohol, but this melts at 125°, does not decompose at 185°, and is less soluble in water. It is suggested that the aminoacetaldehyde obtained by Fischer may be the hydroxymethylene compound

$NH_2 \cdot CH \colon CH \cdot OH$, whereas the product from allylamine hydrochloride has the aldehydic structure $NH_2 \cdot CH_2 \cdot CHO$; α-aminopropaldehyde hydrochloride may be obtained by a similar process. J. J. S.

Preparation of Formiminoethyl Ether. HENRY B. HILL and O. F. BLACK (*Amer. Chem. J.*, 1904, 31, 207—209).—When dry hydrogen chloride is passed into a mixture of mercuric cyanide (1 mol.), mercuric chloride (1 mol.), and ethyl alcohol (2 mols.) diluted with several times its volume of ether at 0°, the *mercury* double salt of formiminoethyl ether hydrochloride, $NH \colon CH \cdot OEt, HCl, HgCl_2$, separates in colourless plates. This compound is comparatively stable and, when heated with aniline, yields diphenylformamidine. It reacts with alcohol with formation of ethyl orthoformate, and can, therefore, be used in place of formiminoethyl ether hydrochloride in the preparation of acetals by Claisen's method.

Zinc cyanide yields a similar double *salt* of formiminoethyl ether hydrochloride which is deliquescent, but silver and potassium cyanides do not furnish compounds of this kind. E. G.

Action of Nitriles on Carboxylic Acids. W. KÖNIG (*J. pr. Chem.*, 1904, [ii], 69, 1—39).—Nitriles react with carboxylic acids to form secondary amides, except in the case of a fatty nitrile and an aromatic acid, when exchange of the cyano- and carboxy-groups takes place (Colby and Dodge, Abstr., 1891, 409). The entrance of negative groups into the molecule should facilitate the reaction, and this is found to be the case.

Chloroacetonitrile and chloroacetic acid react together when heated three hours at 135—140°, forming s-*dichlorodiacetamide*,

$$NH(CO \cdot CH_2Cl)_2,$$

which crystallises from acetone in silvery-white leaflets, and melts and decomposes at 189°. The dust violently attacks the mucous membrane. It is insoluble in ether, sparingly soluble in benzene, chloroform, or light petroleum, readily so in hot water, alcohol, acetone, or acetic acid. Alkalis hydrolyse it, and prolonged boiling with alcohol forms ethyl chloroacetate and chloroacetamide. Chloroacetonitrile and dichloroacetic acid react at 130° to form *chloroacetyldichloroacetamide*,

$$CH_2Cl \cdot CO \cdot NH \cdot CO \cdot CHCl_2,$$

crystallising from a mixture of benzene and light petroleum in star-shaped groups of needles and melting at 98°. Chloroacetonitrile and trichloroacetic acid react at 120° to form *chloroacetyltrichloroacetamide*, $CH_2Cl \cdot CO \cdot NH \cdot CO \cdot CCl_3$, crystallising from light petroleum in leaflets and melting at 80°, dissolving readily in most solvents and deliquescing in moist air, at the same time undergoing partial hydrolysis. *Chlorobromodiacetamide*, $CH_2Cl \cdot CO \cdot NH \cdot CO \cdot CH_2Br$, from chloroacetonitrile and bromoacetic acid at 110°, crystallises from benzene in pearly leaflets and melts and decomposes at 180°.

The symmetrical structure of the secondary amides is proved by the fact that chloroacetonitrile and acetic acid, or acetonitrile and chloroacetic acid, yield the same product, *chlorodiacetamide*,

$$CH_2Cl \cdot CO \cdot NH \cdot COMe,$$

crystallising from benzene in pearly leaflets and melting at 105—106°. In similar manner, *p*-chlorophenylacetonitrile and phenylacetic acid, or phenylacetonitrile and *p*-chlorophenylacetic acid, form p-*chlorodiphenyldiacetamide*, $CH_2Ph\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot C_6H_4Cl$, crystallising from alcohol in white needles and melting at 172°, dissolving sparingly in water, ether, or light petroleum, readily in hot benzene or alcohol.

Succinic acid reacts with succinonitrile at 260°, forming succinimide, probably owing to decomposition of the unstable secondary amide at first formed. No amides were obtained from acetonitrile and trichloroacetic acid, acetonitrile, benzonitrile, or phenylacetonitrile and thioacetic acid, benzoyl cyanide and phenylacetic acid, or from chloroacetonitrile and mandelic acid. Cyanogen bromide and bromo- or cyanoacetic acid also gave no definite reaction.

Nitriles condense with *ortho*-substituted aromatic acids, forming quinazoline derivatives. Secondary amides are probably formed in the first place, and water is then eliminated. Anthranilic acid and phenylacetonitrile at 145° form 4-*keto*-2-*benzyldihydroquinazoline*,

$$C_6H_4<\begin{matrix} N{=}C\cdot CH_2Ph \\ CO\cdot NH \end{matrix},$$

which crystallises from acetic acid in silky, felted needles, melts at 242°, and is insoluble in water, but very soluble in pyridine. Warm solutions of alkali hydroxides dissolve it, forming salts, but no salt with hydrochloric acid could be obtained. 4-*Keto*-2-p-*chlorobenzyldihydroquinazoline*,

$$C_6H_4<\begin{matrix} N{=}C\cdot CH_2\cdot C_6H_4Cl \\ CO\cdot NH \end{matrix},$$

from anthranilic acid and *p*-chlorophenylacetonitrile, softens at 240° and melts and decomposes at 246°. Benzoyl chloride in pyridine solution forms 4-*keto*-2-p-*chlorobenzyl*-3-*benzoyldihydroquinazoline*, which forms white, felted needles, sinters at 170°, and melts at 210°. Succinonitrile and anthranilic acid form 2-*ethylene*-bis-4-*ketodihydroquinazoline*, $C_2H_4\left(C<\begin{matrix} N{-}C_6H_4 \\ NH\cdot CO \end{matrix}\right)_2$, crystallising from acetic acid in minute, yellow needles, very sparingly soluble in all solvents except pyridine, and melting above 310°. Boiling with dilute acetic acid causes it to take up H_2O, which is only lost at 190—200°. It has both acid and basic properties, forming crystalline *sodium*, *copper*, *silver*, and *ferric* salts, and a *platinichloride* $C_{18}H_{16}O_2N_4PtCl_6$ in yellow needles, decomposing above 300°. Anthranilic acid and cyanoacetic acid form cyanoacetanilide; anthranilic acid and benzoyl cyanide form benzoylanthranilic acid. Phthalimide and anthranilic acid form a *compound*, $C_{21}H_{14}O_3N_2$, crystallising from alcohol in white needles, very sparingly soluble in water, readily in alcohol or acetic acid. This is not, as might be expected, *o*-phthaliminobenzanilide, since this, prepared synthetically from phenyl-*o*-aminobenzamide and phthalic anhydride, was found to melt at 205°.

Salicylic acid and phenylacetonitrile form phenylacetamide and a salicylide.

Cyanogen bromide reacts with a hot aqueous solution of anthranilic acid, forming *diphenylguanidine-di*-o-*carboxylic acid*,

$$NH{:}C(NH\cdot C_6H_4\cdot CO_2H)_2,\tfrac{1}{2}H_2O,$$

which crystallises from acetic acid in small, greenish-yellow needles, very sparingly soluble in most solvents, and melting and decomposing at 201°. The metallic salts are crystalline and characteristic. The constitution was established by conversion into 2 : 4-diketotetrahydroquinazoline and anthranilic acid by boiling with alkalis or acids, and by conversion into 3 : 4-dibromoanthranilic acid by bromine. Anthranilamide and cyanogen bromide form *diphenylguanidine-di-o-carboxylamide*, $NH:C(NH \cdot C_6H_4 \cdot CONH_2)_2,H_2O$, crystallising from water in star-shaped groups of needles and melting above 290°, sparingly soluble in most solvents, readily so in glacial acetic acid to a solution with blue fluorescence. Acids or alkalis yield the same products as in the case of the carboxylic acid. The amide forms an orange, crystalline *chromate*, and a *picrate*, $C_{15}H_{15}O_2N_5,C_6H_3O_7N_3$, crystallising from nitrobenzene in yellow, concentrically grouped needles with green fluorescence, and melting above 280°.

Mono- and di-bromo- and nitro-anthranilic acids do not react with cyanogen bromide. C. H. D.

Action of Nitrous Acid on the Amide of Malonic Acid and its Homologues. FLORIAN RATZ (*Monatsh.*, 1904, 25, 55—123).—The action of fuming nitric acid of sp. gr. 1·47—1·50 on an aqueous solution of malonamide yields nitromalonamide, $C_3H_5O_4N_3$ (see Richemann and Orton, Trans., 1895, 67, 1002), which is also obtained by the action of boiled nitric acid on the amide suspended in sulphuric acid, and by the addition of aqueous sodium nitrite to a cold solution of the hydrochloride of the amide; concentrated nitric acid, quite free from nitrous acid, is without action on the amide. Nitromalonamide has strongly acid properties, decomposing carbonates and forming characteristic monobasic salts; the silver salt is white, and not yellow as has been stated. The action of an alkyl iodide on the silver salt yields not a substituted derivative of nitromalonamide, but the latter itself.

In order to compare the various compounds obtained with respect to their power of yielding ammonia when treated with acids or alkalis, the author has used the method of distillation in a current of steam, the amount of ammonia in the distillate being determined from time to time. When acids are used, the substance and acid are heated together for a certain time by means of a current of steam, excess of alkali being then added and the ammonia distilled off in a current of steam; in this case, the effect of the alkali added must be subtracted.

With dilute sulphuric acid, nitromalonamide readily yields 2 mols. of ammonia, but with potassium hydroxide only 1 atom of nitrogen is eliminated readily and the other much more slowly. Water exerts a hydrolysing action on nitromalonamide, yielding the ammonium derivative; besides this, a further action takes place giving rise to:

(1) A small proportion of iso*nitrosomalonamide*,

$$NH_2 \cdot CO \cdot C(:NOH) \cdot CO \cdot NH_2,$$

which separates from 70 per cent. aqueous alcohol in pale yellow needles melting and decomposing at about 175·5°; it is readily soluble in water, ethyl or methyl alcohol, or acetone, and slightly so in ether,

benzene, or chloroform, and has the normal molecular weight in aqueous solution. It yields a *silver* derivative, $C_3H_4O_3N_3Ag$, separating in concentrically-arranged, greenish-yellow needles, a white, amorphous *lead* compound, and a green, crystalline, *copper* derivative. When hydrolysed with dilute acids, it yields two of its nitrogen atoms in the form of ammonia and the third as hydrogen cyanide, whilst with alkalis it yields only 2 mols. of ammonia. When its aqueous solution is left in contact with metallic iron, best powdered, it assumes an intense bluish-violet colour; this reaction is also given with zinc dust and a ferrous salt, or with sodium acetate and a ferrous salt, excess of the latter causing its disappearance. This colour is also destroyed by traces of an acid or alkali, and may hence serve as a very sensitive indicator. The *methyl* derivative, $C_4H_7O_3N_3$, separates from alcohol in needles melting at 143·5—144·5°, and is readily soluble in water or methyl alcohol; when hydrolysed by means of alkalis, it gives up 2 atoms of nitrogen very readily as ammonia, whilst with acids it yields also a third nitrogen atom as hydrogen cyanide; it gives a slight coloration with ferrous salts, but this is probably due to the presence of small quantities of the parent substance. The *ethyl* derivative,

$$C_5H_9O_3N_3,$$

separates from aqueous solution in crystals melting at 150·5—151·5°; it gives no coloration with ferrous salts. The constitution of *iso*nitrosomalonamide was confirmed by synthesising it as follows: ethyl nitrosomalonate was prepared by passing nitrogen trioxide (from arsenious anhydride and nitric acid) into an absolute alcoholic solution of ethyl sodiomalonate until a neutral reaction is obtained; if the gas is passed slowly into the ice-cold solution, yields of 90—95 per cent. can be obtained (see Conrad and Bischoff, Abstr., 1880, 629). The action of alcoholic ammonia on ethyl nitrosomalonate yields the ammonium derivative of *iso*nitrosomalonamide, which, with silver nitrate, gives the silver derivative of *iso*nitrosomalonamide.

Hydrolysis of *iso*nitrosomalonamide with dilute sulphuric acid yields two isomeric *compounds*, $C_3H_4O_4N_2$, which both act as dibasic acids, one hydrogen atom being very strongly acidic in character and the other much less so. Both contain a nitrogen atom capable of yielding ammonia very readily on treatment with acids and less readily with alkalis; the second nitrogen atom is given up in the form of hydrogen cyanide. Both form crystals decomposing at about 139—140°. The two compounds (α- and β-) differ widely in their solubilities in alcohol, and also exhibit differences in their velocities of hydrolysis by means of acid or alkali. Neither alone nor in presence of 1 mol. of sodium hydroxide do these compounds give any characteristic reaction with ferrous salts, but if a little sodium acetate or another mol. of sodium hydroxide is added, an intense violet coloration (in presence of $\frac{1}{2}$ mol. of ferrous sulphate) or a dark blue precipitate (with 1 mol. of ferrous sulphate) is obtained; these dark blue ferrous compounds are not formed if even traces of acid are present, but, when once formed, are very stable, and are not destroyed either by heating or by the addition of a concentrated acid or alkali solution. Both the α- and β-compounds form silver derivatives, $C_3H_3O_4N_2Ag$ and $C_3H_2O_4N_2Ag_2$, and also mono-

methyl compounds. The nature of their isomerism has not been definitely settled, but it is supposed that they are *anti-* and *syn*-forms.

On hydrolysing the methyl derivative of *iso*nitrosomalonamide so as to remove one amino-group, a *compound*, $C_4H_6O_4N_2$, is obtained, which separates from alcohol, or a mixture of alcohol and chloroform, in microscopic rhombohedra melting and decomposing at 137—138°; it is a monobasic acid, and yields a crystalline *silver* compound,

$$C_4H_5O_4N_2Ag,$$

and readily soluble *copper* and *lead* derivatives. When both the amino-groups of the methyl derivative of *iso*nitrosomalonamide are removed by hydrolysis, a dibasic *acid*, $C_4H_5O_5N$, is obtained, which crystallises from benzene in a felted mass of slender needles, melting without decomposing at 90—91°; it is readily soluble in water, methyl or ethyl alcohol, acetone, or ether, and yields an insoluble *lead* salt and a crystalline *silver* salt, $C_4H_3O_5NAg_2,\frac{1}{2}H_2O$; it is identical with the compound obtained by methylating *iso*nitrosomalonic acid.

On oxidising *iso*nitrosomalonamide with acid permanganate, it yields nitromalonamide.

(2) The second product of the action of water on nitromalonamide proved to be a mixture of at least two compounds. The first of these is a *polyamide*, $(C_6H_9O_5N_6)_n$, which separates from aqueous alcohol in yellowish-red crystals, but was not obtained quite free from ash (about 0·3 per cent.); when hydrolysed with acid or alkali, it gives up three-fourths of its nitrogen in the form of ammonia, so that the empirical formula must at least be doubled; on restricted hydrolysis, it yields an *acid* giving a *silver* salt of the composition $(C_6HO_9N_2Ag_4)_n$. Another *compound*, obtained from this mixture, separates from water in microscopic, club-shaped, and drusy, crystalline masses having the composition $(C_6H_{11}O_6N_6)_n$.

(3) Another *compound* separated from the solution obtained by the action of water on nitromalonamide is slightly soluble in water, acetone, methyl or ethyl alcohol, and gives a *silver* derivative, $(C_3H_2O_3N_2Ag)_n$, which was not obtained in a pure state [compare M. A. Whiteley, Trans., 1903, 83, 24]. T. H. P.

The Diureides. Ethyl Homoallantoate. LOUIS J. SIMON (*Compt. rend.*, 1904, 138, 372—374).—Ethyl homoallantoate (compare Abstr., 1902, i, 15), prepared by the direct action of carbamide on ethyl pyruvate, is a white, microcrystalline solid, decomposing at about 200°, insoluble in cold water or most organic solvents, slightly soluble in boiling alcohol, and more so in the presence of pyridine; it is hydrolysed by the action of boiling water into carbamide and ethyl pyruvate, and decomposed by concentrated hydrochloric acid into pyruvic acid and dipyruvyltriureide (compare Abstr., 1903, i, 314); it is slightly soluble in concentrated solutions of ammonia or methylamine, and from the solutions, crystals of homoallantoin (pyruvil) slowly separate; alcoholic or aqueous solutions of potassium carbonate effect a similar change, the potassium derivative of homoallantoin being produced, which is insoluble in the alcoholic, but soluble in the aqueous solution, and readily converted into homoallantoin by hydrochloric acid. M. A. W.

Ureides of Glyoxylic Acid: Allantoin and Allantoic Acid. Louis J. Simon (*Compt. rend.*, 1904, 138, 425—428).—Allantoin dissolves in strong aqueous potassium hydroxide, giving a clear solution which, after a short time, deposits a thick, crystalline precipitate of potassium allantoin, $CO<\begin{matrix} NK \cdot CO \\ NH \cdot CH \cdot NH \cdot CO \cdot NH_2 \end{matrix}$.

After the lapse of a few hours, a further change takes place, and the potassium allantoin is converted to potassium allantoate,

$$CH(NH \cdot CO \cdot NH_2)_2 \cdot CO_2K,$$

which is crystalline, and soluble in water. Allantoic acid can be obtained from this salt as a white, crystalline powder, which decomposes when heated at about 165°. It is very slightly soluble in water, dilute acids, and organic solvents, but dissolves in potassium carbonate solutions, liberating carbon dioxide; it is also soluble in solutions of potassium acetate. Silver allantoate is insoluble in water. Allantoic acid is decomposed by warm water, dissolving therein and giving carbamide and glyoxylic acid; the same decomposition may take place in cold acidified solutions of the potassium salt. If the solution of allantoic acid is heated for a longer period, a certain amount of allantoin is formed. S. S.

Some Compounds of Cuproso-cupric Cyanide with Pyridine, Methylamine, Dimethylamine, and Trimethylamine. Franz M. Litterscheid (*Arch. Pharm.*, 1904, 242, 37—42. Compare Schmidt and Malmberg, Abstr., 1898, i, 547).—A reddish-brown *precipitate* of the composition $Cu_3(CN)_4,5C_5H_5N$ is obtained by adding pyridine to aqueous copper sulphate until the precipitate that forms at first has redissolved, and then adding aqueous potassium cyanide cautiously. Shaking with much water converts it into a green *compound*, $Cu_3(CN)_4,3C_5H_5N$; heating for 24—30 hours at 100° into a yellowish-brown *compound*, $Cu_3(CN)_4,2C_5H_5N$, whilst prolonged heating at 105—110° drives off all the pyridine from it (exposure to the air for days also effects this).

A green *precipitate* or green *crystals*, having the composition

$$Cu_3(CN)_4,4NH_2Me,$$

are obtained by adding aqueous potassium cyanide to aqueous copper sulphate until the precipitate that forms at first has redissolved, and then adding methylamine. Similar green amorphous *compounds*, $Cu_3(CN)_4,4NHMe_2$ and $Cu_3(CN)_4,4NMe_3$, are obtained by using di- and tri-methylamines instead of methylamine. In all three cases, blue compounds containing more than 4 mols. of the base were prepared, but they had no definite composition. C. F. B.

Hydrargyrum Oxycyanatum. E. Holdermann (*Arch. Pharm.*, 1904, 242, 32—36).—Aqueous mercuric cyanide, suitably about 13 per cent. in strength, dissolves freshly precipitated mercuric oxide, when digested with this on the water-bath in proportions corresponding with the formula $3Hg(CN)_2,HgO$, and the crystals which separate when the filtered solution is concentrated have a corresponding composition. No compound in other proportions could be obtained, in spite of the statements in the text-books.

The cyanogen in the substance was estimated by treating it with water and magnesium powder, collecting the hydrogen cyanide which is evolved in aqueous potassium hydroxide, and titrating it with *N*/10 silver solution. Half of the liquid is eventually distilled over from the remaining magnesium, and then some dilute sulphuric acid is added through a stoppered funnel; the hydrogen evolved carries over the last traces of hydrogen cyanide. C. F. B.

Cyano-derivatives of Vanadium. EMIL PETERSEN (*Zeit. anorg. Chem.*, 1904, 38, 342—349).—Details of the preparation of potassium vanadiocyanide, $K_4V(CN)_6,3H_2O$, previously described by the author (Abstr., 1903, i, 612), are given. The *double salt* of potassium pyrovanadate and potassium cyanide, $K_4V_2O_7,4KCN,14H_2O$, prepared by electrolysing a solution of potassium metavanadate and potassium cyanide and then allowing the salt to separate from the solution, which had been concentrated by evaporation, forms white, prismatic crystals, and gradually parts with hydrogen cyanide on exposure to the atmosphere. A. McK.

Synthesis of Hydrocarbons by Organo-magnesium Compounds and Methyl Sulphate. JOSEF HOUBEN (*Ber.*, 1904, 37, 488—489).—Controversial. A reply to Werner (this vol., i, 25). A. McK.

Optically Active Benzene Hydrocarbons. AUGUST KLAGES and RICHARD SAUTTER (*Ber.*, 1904, 37, 649—655).—A large quantity of pure active amyl alcohol, prepared according to Marckwald's method (Abstr., 1901, i, 248) ($[\alpha]_D$ $-5{\cdot}89°$ at 18°), was converted into pure amyl iodide, which has the following constants: sp. gr. 1·5232 at 15°/4°, $[\alpha]_D$ $+5{\cdot}78°$ at 15°, boiling point 148°.

Active *methylpentenylbenzene* (*α-phenyl-γ-methyl-Δ^α-pentene*),

CHPh:CH·CHMeEt,

prepared by the interaction of benzaldehyde with a solution of amyl iodide and magnesium in ether, boils between 110° and 113° under 15 mm. pressure and has $[\alpha]_D$ $+43°$ at 12°. When purified by conversion into the chloride and heating with pyridine, the phenylhexylene boils at 100—103° under 9·5 mm. pressure, has sp. gr. 0·8906 at 15°/4°, and $[\alpha]_D$ $+50{\cdot}3°$ at 15°. It forms a *dibromide*,

CHPhBr·CHBr·CHMeEt,

which crystallises from alcohol in colourless needles, melts at 91—92°, and has $[\alpha]_D$ $+32{\cdot}1°$ at 15° in chloroform solution.

Active *hexylbenzene* (*α-phenyl-γ-methylpentane*),

$CH_2Ph{\cdot}CH_2{\cdot}CHMeEt$,

prepared by reduction with sodium and alcohol, boils at 90—91° under 9 mm. and at 220° under 757 mm. pressure; it has a sp. gr. 0·8644 at 14·5°/4°, $[\alpha]_D$ $+17{\cdot}2°$ at 14·5°, and forms a sulphonic acid, of which the barium salt crystallises in glistening plates. It is not racemised on heating with either sodium ethoxide or alcoholic potash. E. F. A.

Styrenes. IV. Styrenes Derived from Mesitylene. AUGUST KLAGES and CH. STAMM (*Ber.*, 1904, 37, 924—931. Compare Abstr., 1902, i, 611, 666; 1903, i, 19).—Dimethylstyrenes of the type

$C_6H_2Me_3\cdot CH\colon CHR$ may be obtained from the acyl derivatives,

$$C_6H_2Me_3\cdot CO\cdot CHR,$$

by reduction to the carbinol, transformation into the corresponding chloride, and treatment with pyridine. These unsaturated hydrocarbons show no tendency to polymerise, and on treatment with sodium and ethyl alcohol are not reduced to the corresponding saturated hydrocarbons; the reduction may be accomplished by the aid of hydriodic acid and red phosphorus, except in the case of vinylmesitylene, which yields mesitylene and ethane.

The influence of the radicle R in mesityl ketones, $C_6H_2Me_3\cdot COR$, is very pronounced in the decomposition of the ketones by boiling with syrupy phosphoric acid. Acetylmesitylene requires 1 hour, propionylmesitylene 4 hours, *iso*butyrylmesitylene and heptoylmesitylene 8 hours.

The various substituents in the carbinols formed by the reduction of these ketones do not inhibit urethane formation. The following new compounds were prepared:

iso*Butyrylmesitylene* boils at 142° under 20 mm. pressure and has a sp. gr. 0·9664 at 20°/4°; iso*valerylmesitylene* boils at 151° under 20 mm. pressure and has a sp. gr. 0·9394 at 24°/4°; *heptoylmesitylene* boils at 172° under 15 mm. pressure and has a sp. gr. 0·9384 at 17°/4°.

Mesitylethylcarbinol boils at 142° under 14 mm. pressure; *mesityl*iso*propylcarbinol* boils at 149—150° under 19 mm. pressure and has a sp. gr. 0·9727 at 19°/4°; *mesityl*iso*butylcarbinol* boils at 164° under 21 mm. pressure and has a sp. gr. 0·9440 at 24°/4°; *mesitylhexylcarbinol* boils at 194° under 21 mm. pressure and has a sp. gr. 0·9462 at 17°/4°.

Propenylmesitylene boils at 109—110° under 18 mm. or at 223—224° under 745 mm. pressure, has a sp. gr. 0·8988 at 21°/4°, and n_D 1·5229 at 21°; iso*butenylmesitylene* boils at 118—120° under 14 mm. or at 226—227° under 745 mm. pressure, has a sp. gr. 0·8900 at 18·8°/4°, and n_D 1·5162 at 18·8°; the *nitrosochloride* melts at 136°; *pentenylmesitylene* boils at 136° under 22 mm. or at 239—240° under 758 mm. pressure, has a sp. gr. 0·8901 at 20°/4°, and n_D 1·5114 at 20°; the *nitrosochloride* melts at 185°; *heptenylmesitylene* boils at 170—171° under 23 mm. or at 270—272° under 760 mm. pressure, has a sp. gr. 0·8844 at 17°/4°, and n_D 1·5136; the *nitrosochloride* melts at 160°. The *phenylurethane* of mesityl*iso*propylcarbinol melts at 169°. J. J. S.

Direct Reduction of Aromatic Halogen Derivatives by Nickel and Hydrogen. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1904, 138, 245—248).—Aromatic halogen derivatives can be directly reduced to the corresponding hydrocarbon by the action of hydrogen in the presence of reduced nickel under suitable conditions of temperature.

Chlorine Derivatives.—When a mixture of chlorobenzene vapour and excess of hydrogen is passed over reduced nickel at a temperature of 160°, a small quantity of *cyclo*hexane is formed at first, but the nickel chloride, which is simultaneously produced, renders the nickel inert, and no further action takes place until the temperature is raised to 270°, when hydrogen chloride is evolved together with benzene and a small quantity of diphenyl; the probable course of the reaction being (1)

the formation of nickel chloride and its subsequent reduction, (2) the union of the phenyl residues with hydrogen to form benzene or with one another to form diphenyl; more than 40 per cent. of the final product is benzene. *m*-Dichlorobenzene, similarly treated, gives a mixture of 30 per cent. of benzene, 60 per cent. of chlorobenzene, and about 10 per cent. of the unchanged compound. *p*-Dichlorobenzene gives a reduction product consisting of 35 per cent. of benzene and 65 per cent. of chlorobenzene, whilst hexachlorobenzene gives a mixture containing trichlorobenzenes (chiefly 1 : 2 : 4-), dichlorobenzenes, and a small quantity of chlorobenzene and benzene.

Chlorinated aromatic derivatives containing an alkyl or hydroxyl radicle are more readily reduced (compare Liecke, Abstr., 1900, i, 387), chlorotoluene giving a reduction product containing 50 per cent. of toluene, and 2 : 4 : 6-trichlorophenol a mixture of 75 per cent. of phenol with a little chlorophenols (chiefly ortho-), whilst the presence of an amino-group in the aromatic nucleus is even more effective, *o*- and *m*-chloroanilines being reduced at 200° to aniline hydrochloride and aniline. In the case of chloronitrobenzene, simultaneous reduction of the nitro-group (compare Abstr., 1901, i, 195, 638; 1902, i, 701) and replacement of chlorine by hydrogen obtain, the reaction beginning at 180°, and the products being water, aniline hydrochloride, and aniline.

Bromine derivatives, although less readily reduced than the corresponding chloro-derivatives, yield similar products, thus, bromobenzene is reduced at 270° to benzene and diphenyl; 2 : 4 : 6-tribromophenol gives a mixture of phenol, *p*-bromophenol, and 2 : 4-dibromophenol.

Iodine Derivatives.—The reduction of iodobenzene by the action of hydrogen in contact with nickel can only be effected by passing alternately a mixture of iodobenzene and hydrogen, and hydrogen alone over the nickel at 270°, because the nickel iodide cannot be reduced by hydrogen in the presence of iodobenzene.

Marcellin Berthelot (*ibid.*, 248—249) refers to similar results which he obtained in 1868 by reducing aromatic compounds with hydrogen iodide, namely, (1) the production of benzene from chlorobenzene, hexachlorobenzene, or benzene hexachloride, (2) the hydrogenation of benzene, naphthalene, camphene, and terpene. M. A. W.

Crystallographic and Molecular Symmetry of Position Isomeric Benzene Derivatives. F. M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 406—408).—The six isomeric tribromotoluenes have been prepared in a form suitable for measurement; four of them are monoclinic, one rhombic, and one tetragonal, the last two being those with the bromine atoms in the vicinal position. Of the first four, there are two [$Br_3 = 2:3:5$ and $2:4:6$] which form mixed crystals in all proportions. The densities of the monoclinic forms do not greatly differ; the density of the rhombic isomeride is smaller, and that of the tetragonal isomeride still smaller.

The fifteen possible melting point lines of the binary mixtures of the six isomerides were determined. A. McK.

[Sulphur Derivatives of Diphenyl.] KALLE & Co. (D.R.P. 144464).—Tetranitrodiphenyl sulphide (Beilstein and Kurbatoff, Abstr., 1879, 230) is partially reduced on warming with sodium sulphide. When the product is fused with sodium sulphide and either dinitrophenylaminesalicylic acid (Dierbach, Abstr., 1893, i, 211) or 2 : 4-dinitro-4′-hydroxydiphenylamine, greenish-black dyes are produced, dissolving readily in water. No such products are obtained when the original compounds are fused singly with sodium sulphide.

C. H. D.

Direct Hydrogenation of Aniline. Synthesis of *cyclo*Hexylamine and of Two New Amines. PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1904, 138, 457—460).—Aniline is directly hydrogenised in the presence of reduced nickel at 190°, the product consisting of *cyclo*hexylamine, di*cyclo*hexylamine, and *cyclo*hexylaniline in approximately equal proportions. (1) *cyclo*Hexylamine, $C_6H_{11}\cdot NH_2$, the normal product (compare Abstr., 1901, i, 195, 263; 1904, i, 156), is identical with the compound obtained by Baeyer by reducing *cyclo*hexanoxime (compare Abstr., 1894, i, 175), and by Markownikoff by reducing nitro*cyclo*hexane (compare Abstr., 1899, i, 23). It is a colourless liquid with an intense ammoniacal odour recalling that of coniine, boils at 134° (corr.) under normal pressure, has a sp. gr. of 0·87 at 0°/0°, readily absorbs carbon dioxide from moist air to form a characteristic crystalline soluble carbonate; its hydrochloride crystallises in thin needles melting at 206°, very soluble in water or alcohol, slightly so in ether; it is a strong alkali turning litmus blue, and attacking the skin and corks. (2) *Di*cyclo*hexylamine*, $NH(C_6H_{11})_2$, formed from *cyclo*hexylamine according to the following equation, $2C_6H_{11}\cdot NH_2 = NH_3 + NH(C_6H_{11})_2$, is a colourless liquid with a similar, but much less pronounced, odour; it boils at 145° (corr.) under 30 mm. pressure, and at 250° under normal pressure, with slight decomposition and formation of cyclo*hexylaniline*, $NH(C_6H_{11})_2 = H_6 + NHPh\cdot C_6H_{11}$; it solidifies on cooling, forming prismatic crystals, melts at about 20°, has a sp. gr. 0·936 at 0°/0°, is slightly soluble in water, and very soluble in alcohol, ether, or benzene; it is alkaline towards litmus or phenolphthalein, precipitates silver oxide and copper hydroxide from their respective salts, absorbs carbon dioxide to form a crystalline *carbonate*, which is completely dissociated on drying in the air; the *hydrochloride* crystallises in beautiful, white needles, very soluble in water or alcohol, very slightly so in ether. (3) cyclo-*Hexylaniline*, $NHPh\cdot C_6H_{11}$, formed by the partial destruction of the di*cyclo*hexylamine, is a yellow liquid with a faint odour, boils at 171° under 30 mm. and at 275° under normal pressure, with decomposition and formation of diphenylamine,; it has a sp. gr. of 1·016 at 0°/0°, is very soluble in water, and solidifies on cooling, forming brilliant prisms or rhombic plates which melt at about 10°; the *hydrochloride* crystallises in tufts of slender needles, which are very soluble in water or alcohol, and become grey and then green when exposed to the air. *cyclo*Hexylaniline shows the chemical properties both of a fatty and

an aromatic amine, thus, it turns red litmus blue, but does not form a solid carbonate, and gives colour reactions with oxidising agents similar to those afforded by diphenylamine under the same conditions, namely, with concentrated hydrochloric acid and a drop of nitric acid, an intense blue colour changing through violet to green; with dilute sulphuric acid and a drop of chromic acid, a purple colour changing to chestnut-brown; with dilute sulphuric acid and a drop of nitric acid, a reddish-brown colour; with a concentrated solution of iodic acid, a magnificent purple colour changing to deep violet.

By the prolonged action of hydrogen on diphenylamine in the presence of reduced nickel at 190—210°, a liquid was obtained containing an appreciable quantity of *cyclo*hexylaniline and di*cyclo*hexylamine, together with benzene, aniline, and *cyclo*hexylamine.

M. A. W.

Formation of Salts of Aromatic Bases with Dicarboxylic Acids. Otto Anselmino (*Chem. Centr.*, 1904, i, 505—506; from *Ber. Deutsch. pharm. Ges.*, 13, 494—499).—In some of the following instances, the aromatic base combines with the dicarboxylic acid only in one proportion, namely, that of the acid salt. In these cases, variation of the proportions of acid and base does not affect the result either when the salt is prepared by direct combination of the acid and the base or by mixing aqueous, alcoholic, or ethereal solutions of the components; the same salt is also formed at 100° and at the ordinary temperature, and aqueous solutions of the acid are only able to combine with 1 mol. of the base.

Aniline and *p*-anisidine form normal or acid oxalates; the acid salt is converted into the normal salt by the action of boiling alcohol. *p*-Toluidine, methylaniline, *m*-toluidine, mesidine, and methyl-*o*-toluidine also form acid and normal salts, but the former are not affected by boiling with alcohol. Dimethylaniline, pyridine, and quinoline yield only acid oxalates, and with malonic acid, aniline and *p*-toluidine form only acid malonates. Aniline and *p*-anisidine yield acid succinates which are comparatively stable, whilst *p*-toluidine forms a rather unstable acid salt. Methylaniline, dimethylaniline, and pyridine do not combine with succinic acid, and attempts to prepare aniline and *p*-toluidine salts of sebacic acid also failed.

It appears, therefore, that the stronger acids form salts more readily than the weaker, whilst the weaker bases, on the other hand, combine more readily with acids than the stronger.

Aniline oxalate melts at 175°, aniline hydrogen oxalate at 163°, anisidine oxalate at 199°, anisidine hydrogen oxalate at 186°, *p*-toluidine oxalate at 183—184°, *p*-toluidine hydrogen oxalate at 178°, methylaniline oxalate at 113°, dimethylaniline hydrogen oxalate at 141°, pyridine hydrogen oxalate at 151—152°, and quinoline hydrogen oxalate at 105°. Aniline hydrogen malonate melts at 91—92° and *p*-toluidine hydrogen oxalate at 114°. Aniline hydrogen succinate melts at 122°, anisidine hydrogen succinate at 125°, and *p*-toluidine hydrogen succinate at 123—124°.

E. W. W.

Action of Organo-magnesium Compounds on Thiocarbimides and on Carbylamines. II. FRANZ SACHS and HERMANN LOEVY (*Ber.*, 1904, 37, 874—878. Compare Abstr., 1903, i, 334).—*Thiophenylacetanilide*, NHPh·CS·CH_2Ph, obtained from magnesium benzyl bromide and phenylthiocarbimide, crystallises in pale yellow needles melting at 87°. *Thioacetyl*-p-*chloroanilide*, C_6H_4Cl·NH·CSMe, melts at 143°; *thioacetyl*-p-*phenetidide*. OEt·C_6H_4·NH·CSMe, crystallises in yellow plates and melts at 99—100°; *thiopropionyl*-p-*phenetidide* melts at 74—75°, and *thiobenzoyl*-p-*phenetidide* at 127°. All are readily soluble in most organic solvents, and also dissolve in dilute alkalis.

Dithiopropionylbenzidine and magnesium ethyl bromide yield the *compound*, $C_{12}H_8(NH·CSEt)_2$, melting at 228—229°.

Thiobenzoylmethylamide, NHMe·CSPh, obtained from magnesium phenyl bromide and methylthiocarbimide, crystallises in yellow, glistening needles and melts at 79°. *Thioacetylallylamide*, C_3H_5·NH·CSMe, is a yellow oil distilling at 135—136° under 17 mm. pressure. *Thiopropionylallylamide* is also an oil, and distils at 136° under 12 mm. pressure. Its *dibromide* crystallises in colourless needles and melts at 179°. *Thiobenzoylallylamide*, C_3H_5·NH·CSPh, distils at 214—215° under 17 mm. pressure and yields a *dibromide* melting at 208—209°.

Benzaldehyde may be obtained by adding methylcarbylamine to an ice-cold ethereal solution of magnesium phenyl bromide, pouring into water and dilute sulphuric acid, and distilling the product with steam. The reaction is probably $CH_3·N⁚C \rightarrow CH_3·N⁚CPh·MgBr \rightarrow O⁚CHPh$.

J. J. S.

Derivatives of *m*-Xylene. GIORGIO ERRERA and R. MALTESE (*Gazzetta*, 1903, 33, ii, 277—290).—On nitrating *m*-xylene with nitric acid of sp. gr. 1·48, 2 : 4-dinitro-1 : 3-xylene is produced as well as the 4 : 6-dinitro-compound, which is the principal product. 4 : 6-Dinitro-*m*-xylene is very resistant to oxidising agents, and when heated with nitric acid of sp. gr. 1·15 for 3 hours at 155—160°, only one-third is oxidised to form 4 : 6-*dinitro*-m-*toluic acid*, the remainder being unaffected; the acid obtained crystallises from benzene in transparent, yellow scales, melts at 171—171·5°, and gives an *ethyl* ester which crystallises from methyl alcohol in monoclinic prisms [$a : b : c = 1·61662 : 1 : ?$; $\beta = 61°0'57''$] and melts at 61—62°.

4-*Benzoylamino*-6-*nitro*-m-*xylene*, prepared by benzoylating the corresponding base, crystallises from alcohol in white, silky needles melting at 200°. 4-*Benzoylamino*-2-*nitro*-m-*xylene* resembles it, but melts at 236°.

When 4-amino-6-nitro-*m*-xylene is boiled with acetic anhydride, a mixture of mono- and di-acetyl derivatives is obtained. The monoacetyl derivative, $NO_2·C_6H_2Me_2·NHAc$, crystallises from alcohol in monoclinic plates [$a : b : c = 0·66953 : 1 : ?$; $\beta = 79°36'20''$] and melts at 159°. The *diacetyl* derivative, $NO_2·C_6H_2Me_2·NAc_2$, crystallises from benzene in transparent, anorthic, elongated plates [$a : b : c = 1·04676 : 1 : 1·61337$; $\alpha = 93°3'$; $\beta = 80°5'39''$; $\gamma = 64°56'38''$] and melts at 115°. On oxidising either of these compounds with potassium permanganate, 4-*acetylamino*-6-*nitro*iso*phthalic acid* is obtained, partial hydrolysis occurring in the case of the diacetyl derivative; the acid

crystallises from glacial acetic acid in opaque, white needles and melts and decomposes at 264°. 4-*Amino*-6-*nitro*iso*phthalic acid*, prepared by hydrolysing the acetyl derivative, separates from boiling water in small, yellowish-brown crystals, or in nodules of light straw-coloured needles, melts and decomposes at 280°, and gives a *lead* salt existing in a red and a yellow modification; the *dimethyl* ester,

$$NH_2\cdot C_6H_2(NO_2)(CO_2Me)_2,$$

crystallises from methyl alcohol in hard, yellowish-brown, lustrous crystals and melts at 153°.

Methyl 4-*amino*-6-*nitro*-m-*toluate* [Me : CO_2Me : NH_2 : NO_2 = 3 : 1 : 4 : 6 or 3 : 1 : 6 : 4] can be obtained by methylating the residue obtained after extracting 4-acetylamino-6-nitro-*iso*phthalic acid from the product of oxidation of the foregoing acetylnitrotoluidines; it forms red crystals and melts at 128°. W. A. D.

Dibenzylideneacetone and Triphenylmethane. IV. ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1904, **37**, 597—612. Compare Abstr., 1902, i, 380, 769; 1903, i, 811).—The following system of nomenclature is suggested for aminotriphenylmethane derivatives: $OH\cdot CPh_2\cdot C_6H_4\cdot NH_2$, carbinol; $OH\cdot CPh_2\cdot C_6H_4\cdot NH_2,HCl$, carbinol hydrochloride; $CPh_2Cl\cdot C_6H_4\cdot NH_2$, carbinol [carbinyl] chloride, which is unstable, and is immediately transformed into $CPh_2{:}C_6H_4{:}NH,HCl$, the dye salt; $CPh_2Cl\cdot C_6H_4\cdot NH_2,HCl$, carbinol [carbinyl] chloride hydrochloride.

p-Aminotriphenylmethane is best purified by distillation under reduced pressure; it boils at 248° under 12 mm. pressure, and separates from benzene solution in large crystals containing benzene and melting at 83·5°. The acetyl derivative melts at 166—167° (Abstr., 1890, 1141; 1888, 56; 1891, 695), and on oxidation with chromic acid yields the acetyl derivative of the carbinol; when this is hydrolysed with hydrochloric acid, the aminocarbinol hydrochloride is obtained; it crystallises in pale orange-coloured, anhydrous plates; the free aminocarbinol has not been obtained in a crystalline form (compare Baeyer and Löhr, Abstr., 1890, 1141).

p-*Aminotriphenylcarbinyl chloride hydrochloride*, obtained when the carbinol hydrochloride is covered with dry ether and then saturated with dry hydrogen chloride, crystallises in colourless needles which are extremely hygroscopic. It dissolves in alcohol to a red solution, which slowly deposits colourless needles. When heated at 100° in a current of dry hydrogen, it yields the dye salt in the form of a deep orange-red powder which is soluble in chloroform. The *picrate* of the aminocarbinol, obtained by mixing benzene solutions of the components, crystallises in orange-coloured plates, and on treatment with pyridine yields the aminocarbinol.

The red picrate previously described is the picrate of the dye base, and on treatment with pyridine yields the polymeric anhydro-base, $(C_{19}H_{15}N)_2$, which may also be obtained by decomposing the carbinyl chloride and the carbinyl chloride hydrochloride with pyridine. It crystallises from hot pyridine in long, flat, colourless needles, $(C_{19}H_{15}N)_2,3C_5H_5N$, which lose pyridine at 160°. With anhydrous acids, the base gives red salts, but with aqueous acids, colourless or yellow salts of the carbinol.

The *carbinyl thiocyanate* forms a *hydrochloride*,

$$CNS{\cdot}CPh_2{\cdot}C_6H_4{\cdot}NH_2,HCl,$$

which crystallises in colourless needles.

The compound previously (*loc. cit.*) described as *p*-nitrotriphenylcarbinol is really impure *p*-nitrobenzophenone. *p-Nitrobenzophenone chloride*, $NO_2{\cdot}C_6H_4{\cdot}CPhCl_2$, crystallises in yellow, rhombic plates, melts at 56—57°, and reacts with benzene and aluminium chloride yielding p-*nitrotriphenylcarbinyl chloride*, $NO_2{\cdot}C_6H_4{\cdot}CPh_2Cl$, which crystallises from light petroleum in colourless, glistening prisms melting at 92—93°. With alkalis, it yields p-*nitrotriphenylcarbinol* in the form of short prisms melting at 97—98°, and this, on reduction, gives the *p*-aminocarbinol. p-*Nitrotriphenylcarbinyl thiocyanate*,

$$NO_2{\cdot}C_6H_4{\cdot}CPh_2{\cdot}CNS,$$

crystallises from alcohol in colourless needles melting at 114—115°. p-*Nitrotriphenylmethylphenylsulphone*, $NO_2{\cdot}C_6H_4{\cdot}CPh_2{\cdot}SO_2Ph$, crystallises from acetic acid in rhombic plates melting at 167—168°.

Diphenyl-p-*anisylcarbinol anilide*, $OMe{\cdot}C_6H_4{\cdot}CPh_2{\cdot}NHPh$, obtained by the action of diphenylanisylcarbinyl chloride (Abstr., 1903, i, 812) on aniline, crystallises in small plates melting at 138—139°; when heated for 20 hours with benzoic acid and a little benzene, it yields *ωω-diphenylquinonemethane phenylimide*, $CPh_2{:}C_6H_4{:}NPh$; this may be best purified by conversion into its *picrate*, $C_{31}H_{22}O_7N_4$, which crystallises in blackish-violet, flat needles, or the *sulphate*, which crystallises in black needles. The *hydrochloride*, $C_{25}H_{20}NCl$, crystallises in dark plates, and is soluble in hydrochloric acid saturated with ether. The free base crystallises in red prisms, melts at 133—138°, is unimolecular, and combines with sodium hydrogen sulphite to form a colourless sulphonate. It readily combines with water, yielding p-*anilinotriphenylcarbinol*, $NHPh{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, as a colourless syrup which cannot be transformed back into the red quinoneimide. With methyl alcohol, the base yields p-*anilinotriphenylcarbinyl methyl ether*, $NHPh{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OMe$, which crystallises in colourless plates melting at 127°. J. J. S.

Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. Hans Th. Bucherer (*J. pr. Chem.*, 1904, [ii], 69, 49—91. Compare Abstr., 1901, i, 695, 699; 1902, i, 91, 366, 718; 1903, i, 480).—As indicated previously, when treated with sodium hydrogen sulphite solution, amino- and hydroxy-derivatives of the naphthalene series both yield phenolic sulphites, from which alkalis produce phenols, whilst amines are formed with ammonium sulphite. Benzenoid amines and phenols do not give these reactions, with the exception of *m*-diamino- and *m*-dihydroxy-compounds; in these cases, however, the reaction is complicated by secondary reactions, probably of sulphonation.

With the diaminonaphthalenes and sodium hydrogen sulphite, the main reaction consists in the conversion of one amino-group into a sulphite residue, thus, with naphthylene-1 : 8-diamine the 8-amino-α-naphthol sulphite produced is fairly stable, probably owing to the influence of the *peri*-position, and an analysis served to prove the unimolecular ratio of phenol to sulphurous radicle. The isomeric 5-amino-α-naphthol sul-

phite from naphthylene-1 : 5-diamine undergoes partial hydrolytic dissociation, so that 1 : 5-dihydroxynaphthalene is also produced. With dihydroxynaphthalenes, the formation of di-esters appears to be difficult, the mono-esters resulting from the reaction uniting slowly with diazo-compounds.

Although with sodium hydrogen sulphite 5-amino-α-naphthol gives the sulphurous ester of 1 : 5-dihydroxynaphthalene, 8-amino-α-naphthol gives chiefly 8-amino-α-naphthol sulphite. Of the isomeric 8-amino-α-naphthol-4- and -5-sulphonic acids, the 1 : 8 : 4-compound behaves similarly to 5-amino-α-naphthol, yielding the sulphurous ester of 1 : 8-dihydroxynaphthalene-4-sulphonic acid, and the 1 : 8 : 5-compound reacts similarly to 8-amino-α-naphthol, yielding the sulphurous ester of 8-amino-α-naphthol-5-sulphonic acid.

In the replacement of hydroxyl by the amino-group by means of ammonium sulphite and ammonia, with dihydroxy-compounds, the successive replacement of both hydroxy-groups is possible, excepting with certain *peri*-derivatives which display considerable stability towards sodium hydrogen sulphite, and in cases where the orientation of a substituting sulphonic acid radicle prevents reaction. As regards the latter phenomenon, the main conclusions are, that whilst the presence of a *para*-substituent facilitates, that of a *meta*-sulphonic group hinders the sulphite reactions. Thus these reactions occur more or less readily with 1 : 4-, 1 : 5-, 1 : 6-, 1 : 7-, 1 : 8-, 2 : 1-, 2 : 6-, 2 : 7-, and 2 : 8-aminonaphthalenesulphonic acids; with 1 : 4 : 6-, 1 : 4 : 7-, 1 : 4 : 8-, 1 : 5 : 7-, 1 : 6 : 8-, 2 : 1 : 6-, 2 : 3 : 6-, 2 : 3 : 7-, and 2 : 6 : 8-aminonaphthalenedisulphonic acids, and with 2 : 3 : 6 : 8-aminonaphthalenetrisulphonic acid; but reaction is difficult or absent with 1 : 2-, 1 : 3-, 1 : 2 : 4-, 1 : 2 : 5-, 1 : 3 : 7-, and 2 : 4 : 8-aminonaphthalene- and hydroxynaphthalenesulphonic acids. G. D. L.

[*p*-Phenetidine- and *p*-Anisidine-*o*-sulphonic Acid.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 146655).—p-*Phenetidine-* and p-*anisidine*-o-*sulphonic acids*, prepared by heating the hydrogen sulphates of the bases or by boiling *p*-nitrophenetole or *p*-nitroanisole with sodium hydrogen sulphite, crystallise from water, and form crystalline, readily soluble sodium salts. They may be diazotised and combined with β-naphthol, and the azo-compounds thus obtained form red lakes with barium and aluminium hydroxides, &c.

C. H. D.

Hydroxamic Acids. ANGELO ANGELI, FRANCESCO ANGELICO, and FRANCESCO SCURTI (*Gazzetta*, 1903, 33, ii, 296—311).—*Naphthalenesulphohydroxamic acid*, $C_{10}H_7 \cdot SO_2 \cdot NH \cdot OH$, prepared in the same way as benzenesulphohydroxamic acid (Piloty, Abstr., 1896, i, 555), crystallises from water in colourless plates, melts and decomposes at 153°, and is converted by aqueous potassium hydroxide into naphthalene-2-sulphinic acid and nitroxyl, :N·OH, which can be fixed by means of benzaldehyde or piperonaldehyde, benzhydroxamic and piperonylhydroxamic acids being respectively formed; the production of naphthalene-2-sulphinic acid instead of naphthalene-1-sulphinic acid is particularly noteworthy. When naphthalene-1-sulphohydroxamic acid is

hydrolysed by alcoholic sodium ethoxide in presence of nitrosobenzene, the nitroxyl combines with the latter to form nitrosophenylhydroxylamine.

The hydrolysis of naphthalene-1-sulphohydroxamic acid by acids is different to that effected by alkalis, naphthalene-1-sulphonic acid being formed together with a hydroxylamine salt; the latter can be identified by its giving an oxime with piperonaldehyde. The two kinds of hydrolysis are due to the hydrogen ions being operative in the case of acids, and hydroxyl ions in that of alkalis, as shown by the equations:

I. Acids: $R\cdot SO_2\cdot NH\cdot OH + H\cdot OH \longrightarrow R\cdot SO_2\cdot OH + NH_2OH$.

II. Alkalis: $R\cdot SO_2\cdot NH\cdot OH + H\cdot OH \longrightarrow R\cdot SO_2H + NH(OH)_2$.

$\longrightarrow R\cdot SO_2H + :N\cdot OH + H_2O$.

When naphthalene-1-sulphohydroxamic acid is boiled with acetic anhydride, it gives a *diacetyl* derivative, $C_{10}H_7\cdot SO_2\cdot NOAc_2$, which melts at 104° and, like the parent substance, is resolved by alkalis into naphthalene-2-sulphinic acid and nitroxyl.

Benzene-m-*disulphohydroxamic acid*, $C_6H_4(SO_2\cdot NH\cdot OH)_2$, prepared from benzene-*m*-disulphonic chloride, crystallises from benzene with ½ mol. of the solvent and melts at 152°; like the foregoing compound, it liberates nitroxyl in alkaline solution.

Dinaphthalene-1-*sulpho-hydroxamic acid*, $OH\cdot N(\cdot SO_2\cdot C_{10}H_7)_2$, prepared by acidifying a solution containing sodium nitrite and sodium naphthalene-1-sulphinate, crystallises from methyl alcohol, melts at 102°, and is transformed by cold alkalis into the isomeric *dinaphthalene*-2-*sulpho-hydroxamic acid*, which melts at 115° and is also obtained by the direct interaction of nitrous acid and naphthalene-2-sulphinic acid; the final action of alkalis on both acids is to regenerate the parent sulphinic acid.

Dibenzenesulphohydroxamic acid, $OH\cdot N(SO_2Ph)_2$, is converted similarly by cold aqueous sodium hydroxide into nitrous and benzenesulphinic acids, but by warm 80 per cent. sulphuric acid it is resolved into benzenesulphonic acid and hydroxylamine. The different action of alkalis and of acids is explained in the same way as in the case of the simple sulphohydroxamic acids.

Trinaphthalenesulphohydroxamic acid, $NO(\cdot SO_2\cdot C_{10}H_7)_3$, prepared by the action of warm nitric acid of sp. gr. 1·18 on dinaphthalene-1-sulphohydroxamic acid, is a crystalline powder which is almost insoluble in all solvents and darkens at about 270—280°, subsequently melting to a black liquid. It is resolved by alkalis seemingly into nitric acid and naphthalenesulphinic acid, although the latter cannot be isolated owing to its undergoing decomposition. With acids, on the other hand, it affords hydroxylamine. W. A. D.

[Chloronitroaminophenols.] Chemische Fabrik vorm. Sandoz (D.R.-P. 147060).—6-*Chloro*-2-*nitro*-4-*aminophenol*, prepared by the nitration of 6-chloro-4-aminophenol in sulphuric acid solution, melts at 130°. Intensely black dyes are obtained by diazotising it, combining with α-naphthylamine-6- or -7-sulphonic acid, again diazotising, and combining with α-naphthol-4- or -5-sulphonic acid. 4-*Chloro*-6-*nitro*-2-*aminophenol*, prepared by the partial reduction of the corresponding

chlorodinitrophenol and melting at 152°, and the already known 6-chloro-4-nitro-2-aminophenol do not produce this result.

C. H. D.

Separation of *m*- and *p*-Cresols. CHEMISCHE FABRIK LADENBURG (D.R.-P. 148703).—The separation of *m*- and *p*-cresols by partial sulphonation with sulphuric acid is imperfect, and involves the use of large quantities of sulphuric acid. It is found that pure *m*-cresol is rapidly sulphonated on heating with 4 parts of sodium hydrogen sulphate at 100°, the whole solidifying to a mass of crystalline leaflets. *p*-Cresol, on the other hand, is only sulphonated by this method at 160—180°. Crude cresol is therefore heated with sodium hydrogen sulphate at 100—110°, and dissolved in water, when unaltered *p*-cresol separates as an oily layer, and sodium *m*-cresolsulphonate crystallises from the solution. Should the free *m*-cresol be required, superheated steam at 180° is passed into the solution, a temperature of 130—140° being sufficient when free sulphuric acid is employed. C. H. D.

Condensations in presence of Metals and Metallic Chlorides [Benzylphenol]. MARUSSIA BAKUNIN (*Gazzetta*, 1903, 33, ii, 454—460. Compare Abstr., 1903, i, 818).—The condensation between phenol and benzyl chloride, effected by granulated zinc, in various solvents is described, and the best conditions for preparing benzylphenol, $OH{\cdot}C_6H_4{\cdot}CH_2Ph$, are established; benzylphenyl benzoate,

$$OBz{\cdot}C_6H_4{\cdot}CH_2Ph,$$

melting at 86—87°, was prepared by heating benzylphenol with benzoic acid and phosphoric oxide in benzene solution. A similar compound, melting at 155—156°, was obtained from *β*-nitrophenylcinnamic acid, but was not analysed.

In alcoholic solution, zinc condenses benzyl chloride with *p*-aminophenol, giving the *dibenzyl* derivative, $OPh{\cdot}N(CH_2Ph)_2$, which is insoluble in alkali and crystallises from benzene in needles melting at 125—126°; its structure has not yet been determined. W. A. D.

Action of Benzyl Chloride on Naphthols. Formation of Anthracene as a By-product. MICHELE BARBERIO (*Gazzetta*, 1903, 33, ii, 460—466).—Fruitless attempts are described to prepare benzyl-*α*-naphthol and benzyl-*β*-naphthol by the direct interaction of benzyl chloride and the naphthol in presence of zinc chloride (compare following abstracts); in the case of *α*-naphthol, a small quantity of anthracene is formed. W. A. D.

Benzyl-*α*-naphthol and Derivatives. MARUSSIA BAKUNIN and MICHELE BARBERIO (*Gazzetta*, 1903, 33, ii, 467—478).—*Benzyl-α-naphthol*, $OH{\cdot}C_{10}H_6{\cdot}CH_2Ph$, prepared by condensing *α*-naphthol with benzyl chloride in warm benzene solution by means of zinc, crystallises from benzene in white, acicular prisms and melts at 125—126°; the yield is only 30 per cent. that of theory, oily substances, insoluble in alkali, being produced simultaneously. The *acetyl* derivative,

$$OAc{\cdot}C_{10}H_6{\cdot}CH_2Ph,$$

crystallises from benzene in small, snow-white needles and melts at 87—88°; the corresponding *benzoyl* derivative crystallises from alcohol in white needles melting at 102—103°.

With phenyl-*p*-nitrocinnamic acid in presence of phosphoric oxide, benzyl-α-naphthol combines to form the *ester*,

$$CH_2Ph \cdot C_{10}H_6 \cdot O \cdot C_{15}H_{10}O_3N,$$

which crystallises from acetone in long, silky, straw-coloured needles melting at 155—156°; the analogous *compound*, $C_{10}H_7 \cdot O \cdot C_{15}H_{10}O_3N$, of α-naphthol separates from alcohol in flat needles and melts at 126—127°. The compound obtained from benzyl-α-naphthol and salicylic acid forms long, yellow needles and melts at 85—86°.

With nitric acid in glacial acetic acid solution, benzyl-α-naphthol gives a *mononitro*-derivative, which decomposes at 80—90° and has not yet been obtained crystalline. W. A. D.

Benzyl-β-naphthol and Derivatives. MARUSSIA BAKUNIN and GAETANO ALTIERI (*Gazzetta*, 1903, 33, ii, 487—492. Compare preceding abstracts).—*Benzyl-β-naphthol*, $OH \cdot C_{10}H_6 \cdot CH_2Ph$, obtained, with a yield of 25 per cent., by condensing benzyl chloride with β-naphthol by means of zinc in benzene or alcoholic solution, crystallises from glacial acetic acid in long, white needles, and melts at 115—116°; the *acetyl* derivative crystallises from alcohol in well-formed prisms melting at 40°, and the *benzoyl* derivative forms white, silky needles and melts at 95—97°. The *ester*, $CH_2Ph \cdot C_{10}H_6 \cdot O \cdot C_{15}H_{10}O_3N$, prepared by means of phenyl-*p*-nitrocinnamic acid and phosphoric oxide, crystallises from alcohol in needles and melts at 145°. W. A. D.

Preparation of Hydroxydiaryl Sulphides. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 147634).—Hydroxydiaryl sulphides are prepared by heating arylsulphinic acids with phenols or phenol derivatives at 100—150°. Benzenesulphinic acid and phenol form *hydroxyphenyl sulphide*, $C_6H_5 \cdot S \cdot C_6H_4 \cdot OH$, a brown oil with faint, aromatic odour, soluble in water. It is separated from impurities by means of methyl iodide and sodium ethoxide, forming the *methyl* ether, a colourless oil with leek-like odour, boiling at 180—185° under 12 mm. pressure. *Hydroxyphenylsulphide*-o-*carboxylic acid*, prepared from benzenesulphinic acid and salicylic acid, crystallises from dilute acetic acid in small needles and melts at 168°, dissolving sparingly in water and giving a violet coloration with ferric chloride. *Hydroxyphenyl* p-*tolyl sulphide*, obtained from *p*-toluenesulphinic acid and phenol, is a yellow oil, sparingly soluble in water; *hydroxyphenyl*-p-*tolyl-sulphide*-o-*carboxylic acid* crystallises from dilute acetic acid in slightly yellow needles and melts at 162—164°. Similar products are obtained from the cresols. C. H. D.

Dichloromethylene-1 : 2-dioxy-5-propylbenzene and 5-Propylcatechol Carbonate. RAYMOND DELANGE (*Compt. rend.*, 1904, 138, 423—425. Compare Abstr., 1900, i, 289).—When dihydrosafrole (1 mol.) is heated with phosphorous pentachloride (2 mols.) until the evolution of hydrogen chloride ceases and the product submitted to fractional distillation, *dichloromethylene*-1 : 2-*dioxy*-5-*propylbenzene*,

$C_3H_7 \cdot C_6H_3 < ^{O}_{O} > CCl_2$, was isolated as a colourless oil, which fumes in the air and boils at 142—145° under 10 mm. pressure. When boiled with water, the carbonate of propylcatechol is formed as a primary product which is immediately decomposed by the hydrochloric acid present, giving 5-propylcatechol. When the dichloride is allowed to drop slowly into absolute ethyl alcohol, ethyl chloride is evolved and 5-propylcatechol carbonate formed; at the boiling point of alcohol, this carbonate is decomposed giving the free catechol and ethyl carbonate. With phenol, *diphenoxymethylene*-1 : 2-*dioxy*-5-*propylbenzene*,

$$C_3H_5 \cdot C_6H_3 < ^{O}_{O} > C < ^{O \cdot C_6H_5}_{O \cdot C_6H_5},$$

is produced; it is a liquid which boils at 256—258° under 17 mm. pressure. With acetic anhydride, the dichloride yields acetyl chloride and the catechol carbonate; acetic acid gave the same products. The *carbonate* of 5-*propylcatechol*, which is formed in the foregoing reactions, is a liquid boiling at 139—141° under 13 mm. pressure. It reacts with primary and secondary amines giving urethanes of the type $OH \cdot C_6H_3Pr \cdot O \cdot CO \cdot NR_1R$. That derived from aniline melts at 142°, that from *p*-phenetidine at 122°, and that from methylaniline at 110°.

S. S.

Action of Magnesium Phenyl Bromide on Anthraquinone. 9 : 10-Dihydroxy-9 : 10-diphenyldihydroanthracene. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1904, 138, 327—329. Compare Abstr., 1903, i, 200, 348; this vol., i, 83, 346).—By means of Grignard's synthetical method, 9 : 10-*dihydroxy*-9 : 10-*diphenyldihydroanthracene* (9 : 10-*diphenyldihydroanthran*-9 : 10-*diol*) can be obtained from magnesium phenyl bromide and anthraquinone, the following equations representing the reaction:

$$(1)\quad C_6H_4 < ^{CO}_{CO} > C_6H_4 + 2MgPhBr = C_6H_4 < ^{CPh(OMgBr)}_{CPh(OMgBr)} > C_6H_4,$$

$$(2)\quad C_6H_4 < ^{CPh(OMgBr)}_{CPh(OMgBr)} > C_6H_4 + 2HCl = C_6H_4 < ^{CPh(OH)}_{CPh(OH)} > C_6H_4 + MgBr_2 + MgCl_2.$$

Owing to the sparing solubility of anthraquinone in ether, the yield is only 10 per cent. of the theoretical, and the new compound is separated from the unchanged anthraquinone by extraction with boiling methyl alcohol, from which it crystallises in long, colourless, brilliant needles containing alcohol of crystallisation; the crystals are, however, so efflorescent that the amount of alcohol has not been estimated.

The substance, when freed from alcohol, is a white powder melting at 242° (uncorr.); it is very sparingly soluble in most organic solvents, dissolves in concentrated sulphuric acid forming an intense indigo-blue coloration, persistent for several days in the cold, but rapidly becoming orange-yellow when warmed; in glacial acetic acid solution, it exhibits a violet fluorescence, and on the addition of a drop of hydrochloric acid a highly characteristic precipitate in the form of spangles, is produced,

which melts at a much lower temperature than the original compound, and seems to contain chlorine. M. A. W.

Reduction of Triphenylcarbinol and its Homologues to the Corresponding Triphenylmethanes. SALOMON F. ACREE (*Ber.*, 1904, 37, 616—617).—Only hexaphenylethane is obtained when trimethylcarbinol is reduced with stannous chloride (Ullmann and Borsum, Abstr., 1902, i, 755; Gomberg, 1903, i, 244). Triphenylmethane, however, is readily obtained by the reduction of triphenylcarbinol or triphenylbromomethane in boiling alcoholic solution with tin and hydrochloric acid, the latter being gradually added. In the same way, diphenyl-α-naphthylmethane (Lehne, Abstr., 1880, 478) is obtained from diphenyl-α-naphthylcarbinol. C. H. D.

Elimination of Carbon Dioxide from Tertiary Acids by means of Concentrated Sulphuric Acid. (Preparation of Diphenyl-*p*-tolylcarbinol.) AUGUSTIN BISTRZYCKI and JOSEPH GYR (*Ber.*, 1904, 37, 655—664. Compare Abstr., 1901, i, 701 and 716).—*Diphenyl*-p-*tolylcarbinol*, $C_6H_4Me{\cdot}CPh_2{\cdot}OH$, formed quantitatively by the action of cold sulphuric acid on diphenyltolylacetic acid, crystallises from benzene in colourless octahedra, melts at 72—73°, and boils at 227° under 12 mm. pressure. Oxidation with chromic acid mixture converts it into triphenylcarbinol-*p*-carboxylic acid, whilst on reduction diphenyl-*p*-tolylmethane is formed.

p-*Hydroxytriphenyl*-p-*tolylmethane*, prepared by condensing diphenyltolylcarbinol with phenol, crystallises in colourless needles melting at 201°, and dissolves in normal potassium hydroxide on boiling; it forms an *acetoxy*-derivative which crystallises from alcohol in colourless needles and melts at 135°. p-*Acetoxytetraphenylmethane*, $CPh_3{\cdot}C_6H_4{\cdot}OAc$, crystallises in bunches of needles melting at 175°. *Diphenyl*-p-*tolylchloromethane* forms colourless, rhombic plates melting at 99°.

Diphenyl-*p*-tolylcarbinol can also be prepared by Grignard's methods, by the interaction of magnesium phenyl bromide and methyl *p*-toluate in ethereal solution.

p-*Carboxytriphenylacetic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CPh_2{\cdot}CO_2H$, prepared by the oxidation of diphenyltolylacetic acid with permanganate, crystallises in transparent prisms melting at 246—247° and forms a *disilver* salt. When heated with sulphuric acid, the known triphenylmethane-*p*-carboxylic acid is formed. E. F. A.

Derivatives of 2-Chloro-3 : 5-dinitrobenzoic Acid. III. ATTILIO PURGOTTI and C. LUNINI (*Gazzetta*, 1903, 33, ii, 324—335. Compare Purgotti and Contardi, Abstr., 1902, i, 777, 778).—2-o-*Toluidino*-3 : 5-*dinitrobenzoic acid*, $C_6H_4Me{\cdot}NH{\cdot}C_6H_2(NO_2)_2{\cdot}CO_2H$, prepared by boiling 2-chloro-3 : 5-dinitrobenzoic acid with alcoholic *o*-toluidine, crystallises from boiling alcohol in orange-yellow needles, melts at 171—172°, and gives a red, crystalline *potassium* salt with $1H_2O$. The analogous m-*toluidino*- and p-*toluidino*-derivatives are similar and melt at 203° and 220° respectively; the *potassium* salt of the latter crystallises with $2H_2O$.

2-α *Naphthylamino*-3 : 5-*dinitrobenzoic acid* separates from alcohol as a dull red, crystalline powder and melts and decomposes at 226°; the analogous *β-naphthylamine* derivative melts and decomposes at 210°.

2-*Ethylanilino*-3 : 5-*dinitrobenzoic acid*, $NEtPh\cdot C_6H_2(NO_2)_2\cdot CO_2H$, separates from alcohol in minute, yellow crystals melting at 150—151°.

2-*Anthranilo*-3 : 5-*dinitrobenzoic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_2(NO_2)_2\cdot CO_2H,$$

prepared by means of anthranilic acid, separates from glacial acetic acid in small, orange-yellow crystals and melts at 251—252°; the corresponding compounds from *m*- and *p*-aminobenzoic acids crystallise from acetic acid and melt respectively at 273° and 264—265°.

3 : 5-*Dinitrophenylglycine*-1-*carboxylic acid*,

$$CO_2H\cdot C_6H_2(NO_2)_2\cdot NH\cdot CH_2\cdot CO_2H,$$

prepared from 2-chloro-3 : 5-dinitrobenzoic acid and glycine, crystallises from acetic acid in yellow needles and melts at 186—187°; it forms acid and normal salts; the *disilver* salt is a reddish-yellow powder which is stable in the light.

3 : 5-*Dinitro-2-sulphobenzoic acid*, $SO_3H\cdot C_6H_2(NO_2)_2\cdot CO_2H$, prepared by the action of sodium sulphite on 2-chloro-3 : 5-dinitrobenzoic acid, separates from water in minute crystals. W. A. D.

Nitrosobenzoic Acids. FREDERICK J. ALWAY (*Ber.*, 1904, **37**, 333—335).—p-*Nitrosobenzoic acid*, $NO\cdot C_6H_4\cdot CO_2H$, is prepared by reducing *p*-nitrobenzoic acid in alcoholic solution by zinc dust and acetic acid, and adding ferric chloride to the solution of *p*-hydroxylaminobenzoic acid so obtained at a temperature of 45°; it forms a yellow powder, which is very sparingly soluble in the usual solvents and darkens above 250° without melting; with aniline, it combines to form azobenzene-*p*-carboxylic acid.

m-*Nitrosobenzoic acid*, obtained similarly from *m*-nitrobenzoic acid, is a white powder, which darkens above 230°, does not melt, and combines with *p*-toluidine to form toluene-*p*-azo-*m*-benzoic acid. W. A. D.

Stability of Anthranilic Acid and some of its Derivatives. BRONISLAW PAWLEWSKI (*Ber.*, 1904, **37**, 592—596).—The following numbers give the percentage of anthranilic acid decomposed when heated for an hour at the given temperature:

Temp.	150°	160°	170°	180°	190°	200°
Per cent.	23·9	47·7	72·6	76·8	88·3	96·2

The decomposition is complete after 1 hour at 205—210°.

Benzylaminobenzoic acid (Abstr., 1883, 1009) may be obtained by boiling a toluene solution of anthranilic acid with the requisite amount of benzyl chloride.

o-*Nitrobenzylaminobenzoic acid*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2H$, obtained by boiling an alcoholic solution of the constituents, crystallises in golden-yellow needles, melts at 205—206°, and is readily soluble in most organic solvents with the exception of benzene and light petroleum. The corresponding p-*nitro*-derivative melts at 208—210°.

o-*Benzylideneaminobenzoic acid*, obtained from the acid and *o*-nitrobenzaldehyde, crystallises in brick-coloured needles, melts at 167—168°, and dissolves readily in most solvents with the exception of ether and light petroleum. The isomeric m-*nitro*-compound melts at 198—200°. *Cinnamylideneaminobenzoic acid*, $CHPh:CH\cdot CH:N\cdot C_6H_4\cdot CO_2H$, crystallises in golden-yellow plates melting at 163—164°. *Salicylideneaminobenzoic acid*, $OH\cdot C_6H_4\cdot CH:N\cdot C_6H_4\cdot CO_2H$, obtained from anthranilic acid and salicylaldehyde, melts at 202—204°, and *vanillideneaminobenzoic acid*, $OH\cdot C_6H_3(OMe)\cdot CH:N\cdot C_6H_4\cdot CO_2H$, forms a canary-yellow, amorphous mass melting at 172—174° J. J. S.

Preparation of Diphenylaminedicarboxylic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148179).—The production of diphenylamine-2 : 2′-dicarboxylic acid from alkali *o*-chlorobenzoates and ammonia in presence of copper salts (this vol., i, 168) is not a primary reaction, but is due to the action of the anthranilic acid first formed on the unaltered *o*-chlorobenzoate. Other aminobenzoic acids also react with *o*-chlorobenzoic acid when the alkali salts are heated with copper or copper salts at 115—120°. *m*-Aminobenzoic acid forms *diphenylamine*-2 : 3′-*dicarboxylic acid*, melting and decomposing at 281—282°, after previous sintering, and *p*-aminobenzoic acid forms *diphenylamine*-2 : 4′ *dicarboxylic acid*, melting and decomposing at 282—283°, and dissolving more readily in alcohol than its isomerides. C. H. D.

Preparation of Phenylglycine-*o*-carboxylic Acid from Sulphophenylglycine-*o*-carboxylic Acid. KALLE & CO. (D.R.-P. 147228).—The sulpho-group may be eliminated from sulphophenylglycine-*o*-carboxylic acid by electrolysis in alkaline or neutral solution in the manner described for sulphoanthranilic acid (this vol., i, 159), a diaphragm being employed. Very little hydrolysis occurs in slightly acid solutions. C. H. D.

Preparation of Acetylphenylglycine-*o* carboxylic Acid. DANIEL VORLÄNDER & ERICH MUMME (D.R.-P. 147633).—Phenylglycine-*o*-carboxylic acid is not readily acetylated by the ordinary methods, coloured condensation products being formed. The reaction takes place very readily, however, in presence of su'phuric acid or hydrogen chloride, especially when acetic anhydride is employed (compare Vorländer and Weissbrenner, Abstr., 1900, i, 295). C. H. D.

Preparation of Ethyl 2 : 6 : 6-Trimethyl*cyclo*-Δ^2-hexene-4-one-1-carboxylate. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148080).—The sodium compound of ethyl acetoacetate condenses with ethyl *iso*propylideneacetoacetate in cold alcoholic solution, forming sodium ethyl carbonate and *ethyl* 2 : 6 : 6-*trimethyl*cyclo-Δ^2-*hexene*-4-*one*-1-*carboxylate*, $\begin{matrix} CH_2\cdot CMe_2\cdot CH\cdot CO_2Et \\ | \qquad\qquad\quad | \\ CO\cdot CH{=\!=}CMe \end{matrix}$, a colourless or yellow oil, with faint aromatic odour, boiling at 146—148° under 16 mm. pressure. C. H. D.

Alkyloxyalkyl Esters of Salicylic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 146849. Compare Abstr., 1903, i, 485).—Halogen-dialkyl ethers, having the formula X·CHR′·OR (where X = halogen, R and R′ = the same or different alkyls), react with metallic salicylates, forming alkyloxyalkyl salicylates. Thus α-chloroethyl methyl ether and sodium salicylate form *methoxyethyl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CHMe\cdot OMe$, an almost colourless oil with faintly aromatic odour. On heating above 100°, acetaldehyde is evolved. Water, acids, or alkalis hydrolyse it to methyl alcohol, acetaldehyde, and salicylic acid. In similar manner, α-chlorodiethyl ether forms *ethoxyethyl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CHMe\cdot OEt$, a yellow oil, resembling the methoxy-ester. C. H. D.

Reduction of Indigotin and its Bromo-derivatives. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 139567 and 145602).—Indigotin may be reduced to indigo-white by electrolysis at about 70° in presence of sulphites, employing a current density of 4 amperes per sq. dm. The reaction depends on the intermediate formation of hyposulphites. Bromo- and dibromo-derivatives of indigotin may be reduced in similar manner, no portion of the bromine being removed. The leuco-compounds are obtained in the solid and stable form. C. H. D.

o-Phenoxybenzoic Acids. ROBERT FOSSE and A. ROBYN (*Bull. Soc. chim.*, 1904, [iii], 31, 264—267).—5 : 4′-*Dimethyl*-o-*phenoxybenzoic acid*, $C_6H_4Me\cdot O\cdot C_6H_4Me\cdot CO_2H$, prepared by heating *p*-tolyl carbonate with a small quantity of sodium carbonate at 200°, and hydrolysing with sodium hydroxide dissolved in alcohol, the *p*-tolyl ester first produced, is crystalline, and melts at 113—114°. When heated with sulphuric acid, it is converted into 2 : 7-*dimethyldiphenopyrone* [2 : 7-*dimethylxanthone*], $C_6H_3Me{<}^{CO}_{O}{>}C_6H_3Me$, which crystallises from alcohol in light yellow needles and melts at 142°.

3 : 2′-*Dimethyl*-o-*phenoxybenzoic acid*, similarly prepared from *o*-tolyl carbonate, melts at 115°, and, when heated with sulphuric acid at 100°, is converted into 4 : 5-*dimethyldiphenopyrone*, which melts at 172°. T. A. H.

Condensation of Benzilic Acid with Phenols. R. GEIPERT (*Ber.*, 1904, 37, 664—673).—The *lactone* of 2-*hydroxy*-4 : 5-*dimethyltriphenylacetic acid*, $CPh_2{<}^{C_6H_2Me_2}_{CO}{>}O$, produced by the combination of benzilic acid and *o*-xylenol in presence of tin tetrachloride, crystallises from acetic acid in plates, melts at 178°, and is insoluble in cold dilute sodium carbonate; it forms a *monobromo*-derivative crystallising in colourless needles melting at 161°.

The *lactone* of 2-*hydroxy*-3 : 5-*dimethyltriphenylacetic acid*, which crystallises in colourless plates melting at 170°, is obtained from *m*-xylenol; *p*-xylenol, on the other hand, yields 4-*hydroxy*-2 : 5-*dimethyltriphenylacetic acid*, $OH\cdot C_6H_2Me_2\cdot CPh_2\cdot CO_2H$, which crystallises in plates,

decomposes at 236—237°, and is soluble in dilute sodium carbonate; the *acetoxy*-derivative melts and decomposes at 230—231°, and forms a sodium salt, whilst the *monobromo*-derivative forms yellow plates melting at 232—235°.

4-*Hydroxy*-2-*methyl*-5-iso*propyltriphenylacetic acid*, formed on combining benzilic acid and thymol, crystallises in prisms and melts at 197—198°. *Methyl* 4-*methoxy*-2-*methyl*-5-iso*propyltriphenylacetate* forms large, transparent prisms melting at 145—146°.

4-*Hydroxy*-5-*methyl*-2-iso*propyltriphenylacetic acid*, derived from carvacrol, crystallises in prisms and melts and decomposes at 241°; it is a much weaker acid than its isomeride derived from thymol, and forms an easily soluble sodium salt. *Methyl* 4-*methoxy*-5-*methyl*-2-iso*propyltriphenylacetate* forms short prisms melting at 137—138°.

The *lactone* of *diphenyl*-1-*hydroxy*-β-*naphthylacetic acid*,

$$CPh_2<\begin{matrix}C_{10}H_6\\ -CO-\end{matrix}>O,$$

produced by condensation with α-naphthol, crystallises in colourless prisms, softens at 145°, and melts and decomposes at 190°; it forms a *monobromo*-derivative, crystallising in large, transparent crystals melting at 205°, and a *mononitro*-derivative melting at 241°. With β-naphthol, benzilic acid forms the *lactone* of *diphenyl*-2-*hydroxy*-α-(?)-*naphthylacetic acid*, $CPh_2<\begin{matrix}C_{10}H_6\\ -CO-\end{matrix}>O$, which is sparingly soluble in alcohol, melts at 183°, and forms a *monobromo*-derivative, crystallising from acetic acid in long prisms melting at 162—164°. E. F. A.

Action of Nitric Acid on β-Resorcylic Acid and its Derivatives. Franz von Hemmelmayr (*Monatsh.*, 1904, 25, 21—45).—By the action of nitric acid on β-resorcylic acid, the author has obtained styphnic acid and tribasic nitro-β-resorcylic acid, which is very difficult to methylate, but easier to acetylate, although in the latter case only one of the hydroxyl groups is substituted.

Nitro-β-resorcylic acid, $C_7H_5O_6N$, crystallises from water in straw-yellow leaflets or almost colourless needles, containing water of crystallisation and melting at 215°. The following derivatives were prepared: the *disodium*, *trisodium*, *ammonium*, *diammonium*, *barium* ($+3H_2O$), *dibarium* ($+10H_2O$), *silver*, and the *disilver* salts; the *methyl* ester, which crystallises from methyl alcohol in shining leaflets, melting at 167°, and dissolves in ammonia solution, giving an orange-yellow liquid, which, with barium chloride, gives slender, yellow needles of the *compound*, $C_8H_5O_6NBa$. The *acetyl* derivative, $C_9H_7O_7N$, was obtained in impure crystals melting at 150°.

Reduction of nitro-β-resorcylic acid by means of tin and hydrochloric acid yields *amino-β-resorcylic acid hydrochloride*, $C_7H_7O_4N,HCl$, which separates in bluish-green crystals (with $2H_2O$), melting and decomposing at 212—213°; when boiled with water, this hydrochloride yields the free *amino-acid*, which crystallises from water in microscopic prisms ($+H_2O$), melting at 193°, and is soluble in acetic acid, nitric acid, or alkali solution; the *sulphate*, $(C_7H_7O_4N)_2,H_2SO_4$, separates in bunches of acicular crystals, melting and decomposing at 226°.

When heated to above 190°, amino-β-resorcylic acid yields a very

dark blue mass, exhibiting a copper-red lustre ; the alcoholic solution of this substance dyes silk blue, and when mixed with water assumes a red fluorescence, and deposits dark blue flocks ; with hot water, it gives a purple solution, and with alkalis a dark blue liquid, which becomes red on adding hydrochloric acid.

Diazotisation of amino-β-resorcylic acid yields a red, crystalline powder, probably diazo-β-resorcylic acid. T. H. P.

Bismuthoprotocatechuic Acid. PAUL THIBAULT (*Bull. Soc. chim.*, 1904, [iii], 31, 176—178. Compare Abstr., 1902, i, 101 ; 1903, i, 633, 701, 761, and this vol., i, 166).—The author has prepared the bismuthoprotocatechuic acid, $OH \cdot Bi <\substack{O \\ O}> C_6H_3 \cdot CO_2H$, described by Richard (Abstr., 1900, i, 593), by the addition of bismuth lactate, basic nitrate, or oxide to hot aqueous solutions of protocatechuic acid. It crystallises in microscopic, citron-yellow, stellate groups of pyramids, and is soluble in acids and solutions of alkali hydroxides and carbonates. It decomposes at about 250° and has a sp. gr. 2·82 at 16°. With a dilute solution of ferric chloride, it slowly gives a green coloration passing into blue. The *ammonium*, *potassium*, and *sodium* salts are crystalline. The *anilide*, prepared by boiling the acid with aniline, is a greyish-brown powder which is soluble in alkalis and acids, but insoluble in neutral solvents, and is not converted into the aniline salt by prolonged ebullition with water. It decomposes at about 190° and has a sp. gr. 3·19 at 17°. T. A. H.

Crystalline Form of Optically Active Substances, particularly of a Partially Racemic Active Compound. FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1904, [v], 13, 78—85).—The following compounds were obtained by Andreocci (Abstr., 1899, i, 931).

d- and *l*-Acetyldesmotroposantonin, having respectively $[\alpha]_D + 122·6°$ and $- 122·9°$. crystallise in enantiomorphous, hemihedral, orthorhombic forms $[a : b : c = 0·6984 : 1 : 0·9482]$; the racemic mixture of these two, melting at 145°, is probably anorthic, but cannot be obtained in measurable crystals. The active, partially-racemic mixture, melting at 142°, of the *l*-acetyl derivative melting at 154°, and the *d*-acetyl derivative melting at 156° (*loc. cit.*), forms hemimorphic, monoclinic crystals $[a : b : c = 1·5954 : 1 : 0·8602 ; \beta = 79°30']$; its peculiarities have already been noted. The *d*-acetyl derivative melting at 156° is probably orthorhombic.

Of the foregoing compounds, those melting at 156° and at 142° show triboluminescence (compare Andreocci, Abstr., 1899, ii, 719) ; these are the forms which also have an excellent cleavage. W. A. D.

Addition of Acid Sulphites to Cinnamylidenemalonic Acid. ELMER P. KOHLER (*Amer. Chem. J.*, 1904, 31, 243—256).—When an aqueous solution containing molecular proportions of potassium hydrogen sulphite and cinnamylidenemalonic acid is left in the cold for 4 or 5 days, the potassium salts of benzylidenesulphoethylmalonic and benzylidenesulphobutyric acids are produced, and may be separated by means of a strong solution of potassium hydroxide, in which the

salt of the former acid is but sparingly soluble. *Potassium benzylidenesulphoethylmalonate*, $CHPh:CH\cdot CH(SO_3K)\cdot CH(CO_2K)_2$, prepared by gradually adding potassium hydrogen sulphite to a hot solution of potassium cinnamylidenemalonate and pouring the product into cold solution of potassium hydroxide, crystallises in white, lustrous plates and readily suffers decomposition. If its aqueous solution is boiled for a few hours and then acidified, cinnamylidenemalonic acid is precipitated. When dilute hydrochloric acid is added to a boiling solution of the salt, *potassium hydrogen benzylidenesulphobutyrate*,

$$CHPh:CH\cdot CH(SO_3K)\cdot CH_2\cdot CO_2H,$$

is produced, which crystallises in plates; it can be prepared more readily by the gradual addition of potassium sulphite to finely-powdered cinnamylidenemalonic acid suspended in boiling water; when heated with concentrated hydrochloric acid or with alkalis, it is converted into cinnamenylacetic acid. *Benzylidenesulphobutyric acid* crystallises in colourless needles, melts at 76°, decomposes at 125—130°, and is readily soluble in water, alcohol, or acetone; its normal *potassium*, *calcium*, and *barium* salts are described. When this acid is oxidised with potassium permanganate in neutral or alkaline solution, benzoic, malic, and sulphuric acids are formed, but in a solution acidified with phosphoric acid, benzaldehyde, benzoic acid, carbon dioxide, and β-sulphopropionic acid are produced. When bromine is added to a solution of the acid, a blood-red, amorphous precipitate is produced which, if left in contact with the liquid, rapidly becomes colourless; the liquid becomes milky and afterwards clear, and a colourless *substance*, $C_{11}H_{11}O_5SBr$, which appears to be a sultonic acid, separates in small, lustrous crystals; its *methyl* ester crystallises in large, colourless prisms and melts at 148°; the *ethyl* ester melts at 121°. E. G.

Preparation and Properties of Phthalylbenzoylacetone. CARL BÜLOW and BERTHOLD KOCH (*Ber.*, 1904, 37, 577—588. Compare Abstr., 1887, 141).—*Phthalylbenzoylacetone*,

$$\begin{array}{l}CH:CH\cdot C\cdot C(CAcBz) \\ \mid \qquad\qquad \parallel \\ CH:CH\cdot C \text{———} CO\end{array}\!\!>\!O,$$

obtained by the action of phthalyl chloride on sodiobenzoylacetone suspended in dry ether, crystallises from boiling alcohol in colourless, hexagonal plates melting at 175°. The *bisphenylhydrazone*, $C_{30}H_{24}O_2N_4$, melts at 181°, is only sparingly soluble in ether, and dissolves in pure sulphuric acid to a colourless solution which gives the Bülow reaction. The *bis*-p-*nitrophenylhydrazone* crystallises from acetic acid in pale yellow needles melting at 243°, and dissolves in both dilute sodium hydroxide solution and concentrated sulphuric acid. The *bis*-p-*bromophenylhydrazone* crystallises in flat, yellow needles melting at 201°, the *bis-semicarbazone*, $C_{20}H_{18}O_4N_6$, forms glistening, colourless needles, melts at 252°, and dissolves in alcohol, acetic acid, sodium hydroxide solution, and concentrated sulphuric acid. The *dioxime* crystallises in colourless, glistening plates, melts at 63°, and has an odour of camphor.

Hydrolysis with water converts phthalylbenzoylacetone into phthalic acid, benzoylacetone, acetophenone, and acetic acid. Cold alcoholic ammonia transforms the phthalyl derivative into phthal-

amide, benzoylacetone, and benzoylacetonamine (Abstr., 1885, 1237). On reduction with zinc dust and acetic acid, it yields *phthalidylbenzoylacetone*, $C_6H_4<\substack{CH(CHAcBz)\\CO}>O$, which crystallises from hot acetic acid in colourless needles, melting at 119°, and is insoluble in dilute sodium carbonate. With an acetic acid solution of *p*-nitrophenylhydrazine, it yields 5-*phenyl*-1-p-*nitrophenyl*-4-*phthalidyl*-3-*methylpyrazole* in the form of reddish-brown crystals melting at 169°. A second reduction product of phthalylbenzoylacetone is *benzoylacetonebenzyl*-o-*carboxylic acid*, $COMe \cdot CHBz \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, which crystallises from alcohol in small, colourless needles melting at 136°. With *p*-nitrophenylhydrazine, this yields 5-*phenyl*-1-p-*nitrophenyl*-4-*carboxybenzyl*-3-*methylpyrazole* in the form of orange-red needles melting at 219°, and with hydroxylamine hydrochloride and sodium acetate, 5-*phenyl*-4-o-*carboxybenzyl*-3-*methyl*-iso*oxazole* melting at 189—190°. J. J. S.

Addition of Iodine and Potassium Iodide to Organic Compounds containing the Carbonyl Group. ALPHONSO M. CLOVER (*Amer. Chem. J.*, 1904, 31, 256—268).—When a mixture of iodine (4 parts), potassium iodide (3 parts), and benzophenone (8 parts) is heated for a few minutes at 100°, a crystalline product with a golden lustre is obtained. If this substance is recrystallised from chloroform or ether, hexagonal prisms are produced, the sides of which have a golden lustre whilst the bases are dark blue. The compound melts at about 100° and is very soluble in ethyl acetate, acetic acid, or acetone. In dilute solution, it undergoes dissociation into its constituents. When it is shaken with benzene, the iodine and benzophenone are gradually dissolved and the potassium iodide remains as a residue. If the compound is shaken with water, the iodine and potassium iodide slowly pass into solution and the benzophenone is left undissolved. The *compound* crystallised from chloroform has the composition

$$9C_{13}H_{10}O,2KI,7I,CHCl_3,$$

and that crystallised from ether has the composition

$$9C_{13}H_{10}O,2KI,7I,C_4H_{10}O.$$

Benzoic anhydride yields a similar *compound*, $12C_{14}H_{10}O_3,4KI,11I$, which melts at 125—128°. Phthalic anhydride furnishes the *compound*, $2C_8H_4O_3,KI,4I$, which forms dark green, lustrous crystals of irregular shape. With phenylacetic anhydride, the *compound*,

$$5C_{16}H_{14}O_3,3KI,15I,$$

is obtained. The succinic anhydride *compound*, $4C_4H_4O_3,KI,2I$, forms a golden, crystalline mass.

Similar compounds are formed with benzanilide, nitrobenzoyl chloride, and methyl oxalate. Evidence was also obtained of the formation of compounds with acetone and acetic anhydride, but with ethers, alcohols, and phenols no such substances appear to be formed.

E. G.

Disulphones. XIII. Sulphur Derivatives of Unsaturated Ketones. THEODOR POSNER (*Ber.*, 1904, 37, 502—510. Compare Abstr., 1899, i, 604; 1900, i, 5, 16; 1901, i, 14, 88, 474, 703; 1902, i, 82, 220, 296, 622; 1903, i, 242).—In a previous communication (Abstr., 1902, i, 296), the action of mercaptans on unsaturated ketones

was studied, and the influence of the double linking in various ketones on the reactivity of the latter with mercaptans particularly observed. The property possessed by these unsaturated ketones of forming sulphones is now shown to be conditioned, not by the proximity of the ketonic group, but by the presence of the double linkings. The normal ketone reaction becomes less marked with the introduction of alkyl or phenyl groups into the molecule of the unsaturated ketone. Whereas benzylideneacetone, CHPh:CH·COMe, reacts with all mercaptans, dypnone, CMePh:CH·COPh, and benzylideneacetophenone, CHPh:CH·COPh, react with ethyl mercaptan only, and benzaldeoxybenzoin, CHPh:CPh·COPh, does not react at all with mercaptans.

The results are also discussed in the light of Thiele's theory of partial valencies.

βδδ-Triethylsulphonepentane (*ethylideneacetonetriethylsulphone*),

$SO_2Et·CHMe·CH_2·CMe(SO_2Et)_2$,

prepared from ethylideneacetone and ethyl mercaptan, separates from alcohol in glistening, rhombic leaflets and melts at 106°.

βδδ-Tribenzylsulphonepentane (*ethylideneacetonetribenzylsulphone*),

$C_7H_7·SO_2·CHMe·CH_2·CMe(SO_2·C_7H_7)_2$,

prepared from ethylideneacetone and benzyl mercaptan, separates from alcohol as a crystalline powder and melts at 187—188°.

αβγ-Triphenyl-α-ethylsulphonepropane-γ-one (*ethylsulphonebenzyldeoxybenzoin*), $SO_2Et·CHPh·CHPh·COPh$, prepared by oxidising *αβγ-triphenyl-α-thiolethylpropane-γ-one* (*thiolethylbenzyldeoxybenzoin*) in acetic acid solution, separates from alcohol in glistening, colourless needles and melts at 206—207°.

αβγ-Triphenyl-α-thiolbenzylpropane-γ-one (*thiolbenzylbenzyldeoxybenzoin*), $C_7H_7S·CHPh·CHPh·COPh$, prepared from benzyl mercaptan and benzylidenedeoxybenzoin, crystallises from alcohol in needles and melts at 207°. Its chloroform solution, when oxidised, yields *αβγ-triphenyl-α-benzylsulphonepropane-γ-one* (*benzylsulphonebenzyldeoxybenzoin*), $C_7H_7·SO_2·CHPh·CHPh·COPh$, which separates from glacial acetic acid in needles and melts at 252—254°.

α-Phenyl-α-ethylsulphone-δ-dimethylpentane-γ-one (*ethylsulphonebenzylpinacolin*), $SO_2Et·CHPh·CH_2·CO·CMe_3$, prepared by oxidising the oil obtained by interaction of benzylidenepinacolin and ethyl mercaptan, melts at 122—124°, and, with benzyl mercaptan, forms *α-phenyl-α-thiolbenzyl-δ-dimethylpentane-γ-one* (thiolbenzylbenzylpinacolin),

$C_7H_7·S·CHPh·CH_2·CO·CMe_3$,

which crystallises from alcohol in rhombic prisms and melts at 62—63°. The latter compound yields, on oxidation, *α-phenyl-α-benzylsulphone-δ-dimethylpentane-γ-one* (*benzylsulphonebenzylpinacolin*),

$C_7H_7·SO_2·CHPh·CH_2·CO·CMe_3$,

which separates from alcohol in needles and melts at 133—134°.

α-Phenyl-α-thiolphenyl-δ-dimethylpentane-γ-one (*thiolphenylbenzylpinacolin*), $SPh·CHPh·CH_2·CO·CMe_3$, prepared from benzylidenepinacolin and thiolphenol, separates from alcohol in silky needles and melts at 86—88°.

α-Phenyl-α-phenylsulphone-δ-dimethylpentane-γ-one (*phenylsulphonebenzylpinacolin*), $SO_2Ph·CHPh·CH_2·CO·CMe_3$, separates from alcohol as a white powder and melts at 161—164°.

The oil, obtained by interaction of benzylidenepropiophenone and benzyl mercaptan, yielded, on oxidation, *α-benzylsulphone αγ-diphenyl-β-methylpropane-γ-one* (*benzylsulphonebenzylpropiophenone*),

$$C_7H_7\cdot SO_2\cdot CHPh\cdot CHMe\cdot COPh,$$

which crystallises from alcohol in glistening, rhombic prisms and melts at 152—153°.

The condensation product obtained from allyl acetone and benzyl mercaptan yielded, on oxidation, *ββε-tribenzylsulphonehexane* (*allylacetonetribenzylsulphone*), $CMe(SO_2\cdot C_7H_7)_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot SO_2\cdot C_7H_7$, which separates from alcohol in needles and melts at 129—130°. *ββε-Triethylsulphonehexane* (*allylacetonetriethylsulphone*),

$$CMe(SO_2Et)_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot SO_2Et,$$

prepared in an analogous manner, crystallises from alcohol in colourless leaflets and melts at 125—130°.

Allylacetophenone, in an analogous manner, yielded *α-phenyl-ααδ-triethylsulphonepentane* (*allylacetophenonetriethylsulphone*),

$$CPh(SO_2Et)_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot SO_2Et,$$

which melts at 163°.

α-Phenyl-ααδ-tribenzylsulphonepentane (*allylacetophenonetribenzylsulphone*), $CPh(SO_2\cdot C_7H_7)_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot SO_2\cdot C_7H_7$, melts at 225°.

Methylheptenone yielded the two sulphones, *β-methyl-βζζ-triethylsulphoneheptane* (*methylheptenonetriethylsulphone*),

$$SO_2Et\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe(SO_2Et)_2,$$

and *β-methyl-βζζ-tribenzylsulphoneheptane* (*methylheptenonetribenzylsulphone*), $C_7H_7\cdot SO_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe(SO_2\cdot C_7H_7)$, which separates from alcohol in needles and melts at 158°.

Dibenzylidenediethyl ketone yielded *αε-diphenyl-αε-diethylsulphone-βδ-dimethylpentane-γ-one* (*diethylsulphonedibenzyldiethyl ketone*),

$$CO(CHMe\cdot CHPh\cdot SO_2Et)_2,$$

and *αε-diphenyl-αε-dibenzylsulphone-βδ-dimethylpentane-γ-one* (*dibenzylsulphonedibenzyldiethyl ketone*),

$$C_7H_7\cdot SO_2\cdot CHPh\cdot CHMe\cdot CO\cdot CHMe\cdot CHPh\cdot SO_2\cdot C_7H_7,$$

which separates from alcohol in needles, grouped in rosettes, and melts at 209—210°.

The oil, obtained by the condensation of cinnamylideneacetone with mercaptan, yielded on oxidation *α-phenyl-αγ-diethylsulphonehexane-γ-one* (*diethylsulphonephenylbutyl methyl ketone*),

$$SO_2Et\cdot CHPh\cdot CH_2\cdot CH(SO_2Et)\cdot CH_2\cdot COMe.$$

α-Phenyl-αγ-dibenzylsulphonehexane-ε-one (*dibenzylsulphonephenylbutyl methyl ketone*), $C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot CH(SO_2\cdot C_7H_7)\cdot CH_2\cdot COMe$, separates from glacial acetic acid in needles and melts at 265°.

α-Phenyl-αγ-diphenylsulphonehexane-γ-one (*diphenylsulphonephenylbutyl methyl ketone*), $SO_2Ph\cdot CHPh\cdot CH_2\cdot CH(SO_2Ph)\cdot CH_2\cdot COMe$, separates from alcohol in slender needles and melts at 107—109°.

αγ-Ethyldisulphone-αε-diphenylpentane-ε-one (*diethylsulphonephenlbutyl phenyl ketone*), $SO_2Et\cdot CHPh\cdot CH_2\cdot CH(SO_2Et)\cdot CH_2\cdot COPh$, is a viscid oil.

αγ-Dibenzylsulphone-αε-diphenylpentane-ε-one (*dibenzylsulphonephenylbutyl phenyl ketone*),

$$C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot CH(SO_2\cdot C_7H_7)\cdot CH_2\cdot COPh,$$

was also prepared.

αγ-Dithio-phenyl-αε-diphenylpentane-ε-one (*dithiolphenylphenylbutyl phenyl ketone*), $SPh \cdot CHPh \cdot CH_2 \cdot CH(SPh) \cdot CH_2 \cdot COPh$, melts at 102°.

A. McK.

Preparation of *o*-Nitrophenyllactoketone [? *o*-Nitro-α-hydroxybenzylacetone]. Société chimique des usines du Rhône anct. Gilliad, P. Monnet, & Cartier (D.R.-P. 146294).—*o*-Nitrobenzaldehyde condenses with acetone in presence of alkaline compounds, such as sodium sulphite or trisodium phosphate, the reaction taking place at the ordinary temperature or when cooled by ice. A purer product and better yield are obtained than by employing alkali hydroxides as the condensing agent.

C. H. D.

Phenylbenzoquinone [Diphenylquinone] and Derivatives of Diphenyl. Fritz Fichter and August Sulzberger (*Ber.*, 1904, **37**, 878—884. Compare Borsche, Abstr., 1900, i, 25, 594; H. B. Hill, *ibid.*, 392).—*o*-Aminodiphenyl (Huebner, *Annalen*, 1881, **209**, 349) may readily be obtained by reducing the corresponding nitro-derivative with stannous chloride and concentrated hydrochloric acid; on oxidation with manganese dioxide and sulphuric acid, it gives an 11 per cent. yield of diphenylquinone melting at 114°. The corresponding diphenylquinhydrone melts at 177°.

3-*Nitro*-4-*acetylaminodiphenyl* is readily obtained by the action of fuming nitric acid on an acetic acid solution of *p*-acetylaminodiphenyl; it crystallises from alcohol in yellow needles melting at 132°, and, on reduction with tin and hydrochloric acid, yields 5-*phenyl*-2-*methylbenziminazole*, $C_6H_3Ph{<}{\overset{NH}{\underset{N}{}}}{>}CMe$, in the form of colourless plates melting at 116°.

3-*Nitro*-4-*aminodiphenyl*, obtained by the hydrolysis of the acetyl derivative with alcoholic potash, crystallises in red needles melting at 167°, and, on treatment with sulphuric acid and ethyl nitrite, yields 3-nitrodiphenyl melting at 58·5°; Jacobson and Loeb (*Ber.*, 1903, **36**, 4082) give 61°.

3-*Acetylaminodiphenyl* melts at 148°.

3 : 5-*Dinitro*-4-*acetylaminodiphenyl*, obtained as a by-product in the preparation of the mononitro-derivative, crystallises from acetic acid or nitrobenzene in pale yellow needles melting at 240—241°; when reduced with tin and hydrochloric acid, it yields 7-*amino*-5-*phenyl*-2-*methylbenziminazole*, $NH_2 \cdot C_6H_2Ph{<}{\overset{NH}{\underset{N}{}}}{>}CMe$, melting at 94°.

3 : 5-Dinitro-4-aminodiphenyl crystallises from alcohol in orange-yellow needles melting at 233°.

J. J. S.

Halogen Derivatives of Tertiary Bases of the Anthraquinone Series. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 146691).—Tertiary dialkylaminoanthraquinones (Abstr., 1903, i, 498) react with halogens without removal of the alkyl groups. In presence of an excess of halogen, additive compounds may also be formed.

A solution of α-dimethylaminoanthraquinone in hydrochloric acid reacts with bromine (4 atoms) forming a yellow, crystalline *perbromide*,

from which 2 atoms of bromine may be removed by ammonia or sodium hydrogen sulphite, forming 1-*bromo*-4-*dimethylaminoanthraquinone*; this crystallises from pyridine or methyl alcohol in garnet-red leaflets and melts at 178°, and forms crystalline salts with acids. If only 2 atoms of bromine are employed, one-half of the original compound is converted into the perbromide, which reacts on warming to 80° with the remaining unaltered base, forming the bromo-derivative. 4 : 8-*Dibromo*-1 : 5-*tetramethyldiaminoanthraquinone*, from 1 : 5-tetramethyldiaminoanthraquinone, crystallises from pyridine in orange-red leaflets with green reflex, melts at 236°, and forms colourless salts with acids. Excess of bromine forms a crystalline perbromide. *Bromo*-1-*nitro*-8-*dimethylaminoanthraquinone* crystallises from pyridine in brown, glistening needles and melts at 198°. Its salts are decomposed by water. *Bromodimethylaminoanthraquinone*-1-*sulphonic acid* is sparingly soluble in water, and is less basic than the unbrominated acid. 1-Chloro-4-dimethylaminoanthraquinone, prepared by the action of hydrochloric acid and potassium chlorate on 1-dimethylaminoanthraquinone, melts at 172° (compare *loc. cit.*). C. H. D.

Compounds of Anthraquinone with Aromatic Amines. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 148079).—Anthraquinone condenses with aromatic amines, forming compounds in which the ketonic oxygen is probably replaced by the aminic residue. Thus, when anthraquinone is heated with *p*-toluidine and boric acid, a *compound* is obtained, which dissolves in cold, concentrated sulphuric acid to a colourless solution with blue fluorescence, and crystallises from pyridine in golden leaflets or thick, glistening crystals containing pyridine. Anthraquinone and aniline form a mixture of two compounds, one of which, forming thick crystals, is converted on further heating with aniline into the second compound, which dissolves in concentrated sulphuric acid, the solution becoming blue, and then green with an intense blue fluorescence, on warming. C. H. D.

Anthraquinone-1-sulphonic Acid. Max Dünschmann (*Ber.*, 1904, 37, 331—333. Compare Iljinsky, this vol., i, 176, and Schmidt, *ibid.*, i, 256).—It is shown that anthraquinone-1-sulphonic acid is always formed in small quantities in the normal sulphonation of anthraquinone; details are given for separating it from its congeners by taking advantage of the greater solubility of its sodium salt compared with that of the sodium 2-sulphonate and 2 : 6-disulphonate in strongly alkaline solution at 50—55°. W. A. D.

Anthraquinone-1-sulphonic Acid. Carl Liebermann and Bernhard Pleus (*Ber.*, 1904, 37, 646—648).—In connection with Dünschmann's (preceding abstract) recent discovery that commercial anthraquinone-2-sulphonic acid also contains small quantities of the 1-sulphonic acid, it is pointed out that Liebermann and Bischof (Abstr., 1880, 399) had previously obtained small quantities of the barium salt of anthracenecarboxylic acid melting at 245°, which was presumably derived from anthraquinone-1-sulphonic acid present in the commercial

product. It is now shown that this barium salt is easily prepared from the pure anthraquinone-1-sulphonic acid. E. F. A.

Oxidation Products of Quinizarin. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 146223).—Quinizarin is oxidised by heating under pressure with solutions of sodium carbonate, phosphate, borate, acetate, &c., at 120°, forming a mixture of an oxidation product and its leuco-base. The ketonic group appears to exert an oxidising action, being itself reduced. The leuco-compound is converted into the blue oxidation product by boiling its solution with sodium hydroxide. A soluble and an insoluble compound are obtained, the latter predominating at higher temperatures. The insoluble sodium salt may be filtered off and decomposed by acids, forming a *compound*, $C_{28}H_{12}O_8$, which crystallises from quinoline in yellowish-red needles and dissolves in sulphuric acid to a bluish-violet solution. The bluish-violet alkali salts are sparingly soluble in water. On acidifying the filtrate from the sodium salt, a *compound*, $C_{28}H_{14}O_8$, is precipitated, which crystallises from nitrobenzene in long, orange needles, dissolving in sulphuric acid to a reddish-violet solution, and in alkali hydroxides to blue solutions. Both compounds are very sparingly soluble in organic solvents, and their aqueous solutions show characteristic spectra on the addition of boric acid. C. H. D.

Derivatives of Menthylxanthic Acid and Menthenes from Different Sources. L. A. Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1116—1179).—*Methyl menthylxanthate*, $C_{10}H_{19}O{\cdot}CS_2Me$, obtained by the action of methyl iodide or sulphate on sodium menthylxanthate, crystallises from alcohol in almost colourless, slender needles, or from a mixture of ether and alcohol in large prisms melting at 39°; it is readily soluble in ether, benzene, toluene, or chloroform, slightly so in methyl or ethyl alcohol, and has the normal molecular weight in freezing benzene or acetic acid, and $[\alpha]_D$ $-79{\cdot}47°$ in benzene, $-80{\cdot}02°$ in ethyl acetate, and $-80{\cdot}72°$ in chloroform. On dry distillation, it is decomposed according to the equation: $C_{10}H_{19}O{\cdot}CS_2Me = C_{10}H_{18} + CSO + SHMe$.

The *menthene* thus obtained boils at 167·9° under 751 mm. pressure, has $[\alpha]_D$ $+116{\cdot}74°$, sp. gr. 0·8122 at 20°/4°, and n_D 1·45242 at 20°, this value giving the normal molecular refraction for a compound with one ethylene linking; it exhibits normal cryoscopic behaviour in benzene. Its *nitrosochloride*, $C_{10}H_{18}{\cdot}NOCl$, crystallises from a mixture of chloroform and methyl alcohol in thin, colourless needles, and melts at 111—112° when very slowly heated, or as high as 127° when quickly heated; it is readily soluble in chloroform, and, to a slight extent, in benzene, toluene, or ether, but practically insoluble in solvents containing hydroxyl; it has $[\alpha]_D$ $+230{\cdot}1°$ in benzene, $+192{\cdot}3°$ in chloroform, and $+183{\cdot}1°$ in ethyl acetate.

Ethyl menthylxanthate, $C_{10}H_{19}O{\cdot}CS_2Et$, prepared from the corresponding sodium salt and ethyl iodide, is obtained as a pale yellow, viscous liquid, which solidifies, on cooling, to a crystalline mass melting at about 9°; it is readily soluble in ether, benzene, toluene, or chloro-

form, and slightly so in methyl or ethyl alcohol; it has the normal molecular weight in freezing benzene, a sp. gr. 1·0192 at 21°/4°, $[\alpha]_D$ −60·10°, and n_D 1·52761 at 21°. It decomposes, on heating, in a similar manner to the methyl derivative, and the menthene obtained boils at 167·4—167·8° under 750 mm. pressure and has the following constants: sp. gr. at 20°/4°, 0·8120, $[\alpha]_D$ +116·16°, n_D = 1·45227 at 20°.

Menthyldixanthide, $S_2(CS\cdot O\cdot C_{10}H_{19})_2$, prepared by the action of iodine on sodium menthylxanthate, separates from a mixture of toluene and ethyl acetate in yellow, rhombic crystals [$a:b:c$ = 0·7207 : 1 : 1·2788] melting at 92·5—93°; it is readily soluble in benzene, toluene, chloroform, or ether, has the normal molecular weight in freezing benzene, $[\alpha]_D$ −231·4° in benzene, −286·10° in toluene, −286·88° in chloroform, and −289·44° in ethyl acetate. A menthyldixanthide with similar properties is obtained by the action of copper sulphate on sodium menthylxanthate. On distillation, menthyldixanthide yields hydrogen sulphide, carbon oxysulphide, menthene, and menthol. The mode of decomposition is hence quite different from that of diethylxanthide (see Debus, *Annalen*, 1853, **72**, 4, and 1854, **75**, 122).

Menthylxanthic thioanhydride, $(C_{10}H_{19}O\cdot CS)_2S$, prepared by the interaction of methyl or ethyl chlorocarbonate and sodium menthylxanthate, $2C_{10}H_{19}O\cdot CS_2Na + OR\cdot COCl = (C_{10}H_{19}O\cdot CS)_2S + OR\cdot COSNa + NaCl$, separates from a mixture of benzene and alcohol in greenish-yellow, slender crystals or from a mixture of ether and benzene in large, rectangular plates melting at 148—149°; the crystals belong to the rhombic system, and are apparently sphenoidally hemihedral [$a:b:c$ = 1·4469 : 1 : 1·4708); it is readily soluble in ether, benzene, toluene, and chloroform, and, to a less extent, in alcohol, and it exhibits normal cryoscopic behaviour in freezing benzene; $[\alpha]_D$ in benzene solution has the value −53·79°.

When heated together, sodium menthylxanthate and benzoyl chloride react according to the equations, $2C_{10}H_{19}O\cdot CS_2Na + COPhCl = (C_{10}H_{19}O\cdot CS)_2S + COPh\cdot SNa + NaCl$ and $COPhCl + COPh\cdot SNa = NaCl + (COPh)_2S$. Menthylxanthic thioanhydride, when heated, decomposes thus: $(C_{10}H_{19}O\cdot CS)_2S = C_{10}H_{18} + C_{10}H_{19}\cdot OH + COS + CS_2$.

Menthylxanthamide, $C_{10}H_{19}O\cdot CS\cdot NH_2$, prepared by the action of alcoholic ammonia on menthyldixanthide or on menthylxanthic thioanhydride or, best of all, on methyl menthylxanthate, separates from a mixture of benzene and light petroleum in slender needles, or on slow cooling, or from a mixture of alcohol and ether, in large, monoclinic prisms melting at 144—145°, and dissolving readily in alcohol, benzene, ether, or chloroform, and very slightly in light petroleum; in the dark, the crystals exhibit triboluminescence. It has the normal molecular weight in freezing acetic acid or benzene, and $[\alpha]_D$ −120·78° in benzene, −121·58° in toluene, −115·90° in ethyl acetate, −110·99° in dimethylaniline, and −113·17° in alcohol. On heating with alcoholic potassium hydroxide, menthylxanthamide is decomposed according to the equation: $C_{10}H_{19}O\cdot CS\cdot NH_2 + KOH = C_{10}H_{19}\cdot OH + KSCN + H_2O$; this is similar to the hydrolysis of ethylxanthamide (Debus, *loc. cit.*). On heating, menthylxanthamide decomposes, thus: $C_{10}H_{19}O\cdot CS\cdot NH_2 =$

$C_{10}H_{18} + NH_3 + CSO$, whilst ethylxanthamide yields ethyl mercaptan, and cyanic and cyanuric acids: $OEt\cdot CS\cdot NH_2 = SHEt + CHON$.

When heated, *aβ*-diphenyl-*γ*-*l*-menthyliminoxanthide is resolved according to the equation: $NPh{:}CPh\cdot S\cdot CS\cdot O\cdot C_{10}H_{19} = SH\cdot CPh{:}NPh + COS + C_{10}H_{18}$. The menthene thus obtained possesses approximately the same properties as menthenes prepared by other modifications of the xanthic method. The author concludes that this menthene is an individual compound, and is obtained from menthol without isomeric change taking place.

Menthene nitrosochloride possesses double the normal molecular weight in freezing benzene, and the author ascribes to it the constitution

$$CH_2{<}{}^{CHMe-CH_2}_{CH_2\cdot CPr^{\beta}Cl}{>}CH\cdot NO\cdot NO\cdot CH{<}{}^{CH_2-CHMe}_{CPr^{\beta}Cl\cdot CH_2}{>}CH_2.$$

On heating menthene nitrosochloride, it loses a molecule of hydrogen chloride and yields nitrosomenthene, the ketone, of which this is the oxime, being obtained by heating with dilute hydrochloric acid; this ketone, menthenone, gives menthol on reduction. It is hence possible to start from menthol, and, passing successively through menthylxanthic ester, menthene, menthene nitrosochloride, nitrosomenthene, and menthenone, to obtain again the original menthol.

On comparing menthenone with pulegone, it will be seen that the constitution of the former is probably to be represented by the formula $CHMe{<}{}^{CH_2-CO}_{CH_2\cdot CH}{\gg}C\cdot CHMe_2$.

When reduced by means of sodium in alcoholic solution, menthene nitrosochloride yields *l*-menthylamine.

Menthene obtained by the xanthic method gives, with hydrogen bromide, mainly tert.-*menthyl bromide*,

$$CHMe{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}CBr\cdot CHMe_2\ (?).$$

The relationship existing between the various menthol derivatives is discussed and the following conclusions, in addition to those already given, are drawn: (1) the different xanthic derivatives of menthol are capable of decomposing readily at high temperatures, yielding one and the same menthene, possessing high optical activity. (2) All attempts to discover non-homogeneity in this menthene are fruitless. (3) The menthenes obtained from *l*-menthol by means of halogen hydracids consist mainly of *d*-Δ^3-menthene, giving *d*-nitrosochlorides. (4) The menthenes obtained from *l*-menthol by means of acid dehydrating agents contain little Δ^3-menthene, but consist mainly of an isomeride in which the double linking has a different position. T. H. P.

An Isomeride of Borneol, β-Campholenol, and some Derivatives. AUGUSTE BÉHAL (*Compt. rend.*, 1904, 138, 280—282. Compare Abstr., 1902, i, 419).—*β-Campholenol*,

$$\begin{matrix} CMe_2\cdot CMe \\ | \\ CH_2-CH_2 \end{matrix}{>}C\cdot CH_2\cdot CH_2\cdot OH,$$

produced by reducing inactive ethyl campholate with sodium and alcohol (compare Bouveault and Blanc, Abstr., 1903, i, 597, 673, 730), is a liquid with a faint odour of camphor, boiling at 215—216° under

760 mm. pressure; it has a sp. gr. 0·9231 at 0° and 0·9096 at 20°, and n_D 1·47101 at 20°. *Campholenyl formate*, prepared by the action of acetic and formic anhydrides on the alcohol, boils at 215—216°, and has a sp. gr. 0·9800 at 0° and 0·9718 at 20°, and n_D 1·45742 at 20°. *Campholenyl acetate* boils at 228—229°, and has a sp. gr. 0·9518 at 0° and 0·9355 at 20°, and n_D 1·45562 at 22°. *Campholenyl butyrate* boils at 252—254° and has a sp. gr. 0·9660 at 0° and 0·9581 at 20°.

When β-campholenol is boiled with dilute sulphuric acid, it is converted into an isomeric internal ether, campholan oxide, $C_{10}H_{18}O$, which boils at 180—182°, has a sp. gr. 0·9303 at 0° and 0·9173 at 19°, and n_D 1·46071 at 19°. The mechanism of the reaction whereby this compound is formed from the alcohol appears to be (1) the breaking down of the ethylenic union by the fixation of the elements of a molecule of water, (2) the dehydration of the γ-glycol thus produced, for this compound, *β-campholan-αβ-diol*, $CH_2<\begin{matrix}CMe_2\cdot CMe(OH)\\ CH_2-CH\cdot CH_2\cdot CH_2OH\end{matrix}$, prepared by reducing inactive campholenolactone by Bouveault and Blanc's method, is crystalline, melts at 145°, is slightly soluble in light petroleum, soluble in alcohol or benzene, and yields *campholan oxide*, $CH_2<\begin{matrix}CMe_2\cdot CMe-O\\ CH_2-CH\cdot CH_2\end{matrix}>CH_2$, on boiling with dilute sulphuric acid. *β-Campholan-αβ-diol* can also be obtained by the hydrogenation of dehydrocampholenolactone, $CH_2<\begin{matrix}CMe_2\cdot CMe\cdot O\\ CH_2-C=CH\end{matrix}>CO$, or ethyl ketocampholenate, $CH_2<\begin{matrix}CMe_2\cdot CMe\text{———}\\ CH_2-C(CH_2\cdot CO_2Et)\end{matrix}>O$. M. A. W.

Constitution of Camphor. GIUSEPPE ODDO (*Ber.*, 1904, 37, 511—515).—A claim for priority. The author points out that he was the first to indicate the possibility of formulating camphor with two alicyclic rings, united to one another in a position different from the ortho-position. At the time when the author's formula for camphor was submitted (1891), it sufficed to account satisfactorily for the relationships between camphor and the camphor derivatives then known. A. McK.

Ethylidenecamphor. Ethylhomocamphoric Acid. JULES MINGUIN (*Compt. rend.*, 1904, 138, 577—579).—Ethylcamphor is prepared from methyl ethylcamphocarboxylic acid by heating at 180—200° with alcoholic potash; it boils at 107—110° under 10 mm. pressure and has $[\alpha]_D$ + 40° in alcoholic solution. Bromination of ethylcamphor in carbon disulphide solution yields *monobromoethylcamphor*, a liquid which boils and partially decomposes at 115—120° under 10 mm. pressure. When boiled with alcoholic potash, this yields *ethylidenecamphor*, $C_8H_{14}<\begin{matrix}C:CHMe\\ CO\end{matrix}$, as a liquid which boils at 110—115° under 10 mm. pressure, and has $[\alpha]_D$ + 113° in alcoholic solution. The rotatory power of ethylidenecamphor is therefore considerably greater than that of ethylcamphor, a relation which has already been recorded in the case of methylcamphor and methylenecamphor (Abstr.,

1903, i, 428). During the preparation of ethylcamphor from the methyl ethylcamphocarboxylate, a certain amount of ethyl-β-homocamphoric acid is formed. The substance is soluble in ether, melts at 135—140°, and has $[\alpha]_D + 39{\cdot}65°$ in alcoholic solution. S. S.

Essential Oil of Boldo. E. TARDY (*J. Pharm. Chim.*, 1904, [vi], 19, 132—136).—Dried leaves of *Boldoa fragrans* yield rather less than 2 per cent. of essential oil. of a greenish-yellow colour, having the sp. gr. 0·876 at 15° and $\alpha_D - 6°30$ in a 10 cm. tube. The oil contains small proportions of eugenol, cumic aldehyde, and acetic esters. By distillation, the presence of a dextrorotatory and of a lævorotatory terpene, the latter in considerable amount, and of an inactive terpineol was proved. A lævorotatory sesquiterpene was also obtained, which was, however, probably produced during the distillation. G. D. L.

South American Orange Oil. JOHN C. UMNEY and CHARLES T. BENNETT (*Pharm. J.*, 1904, [iv], 18, 217—218).—An account is given of an orange oil of unknown origin imported from Buenos Ayres. The characters of this oil resembled those of orange-leaf oil more closely than those of orange-flower oil, and it contained only traces of methyl anthranilate. It had a sp. gr. 0·887 and $\alpha_D + 2°$. It contained 36·5 per cent. of esters (calculated as linaloyl acetate) and 38·4 per cent. of free alcohols (calculated as geraniol), or total alcohols 67·1 per cent. On distillation under atmospheric pressure, it yielded 5 per cent. below 190°, 12 per cent. below 195°, 25 per cent. below 200°, 35 per cent. below 205°, 54 per cent. below 210°, 65 per cent. below 215°, 80 per cent. below 220°, and 20 per cent. above 220°. The sp. gr., α_D, and n_D are given of each of the various fractions obtained by distillation under reduced pressure. The oil was found to contain pinene, dipentene, linalool, geraniol, and furfuraldehyde. E. G.

Constitution of Gutta-percha Resin. CARL O. WEBER (*Chem., Centr.*, 1904, i, 517—518; from *Gummi-Zeit.*, 18, 342—343. Compare Abstr., 1902, i, 552).—It is very doubtful whether the constitution of gutta-percha resin is represented by Tschirch's formula (this vol., i, 76) which contains hexane rings, since gutta-percha itself, like caoutchouc, is a polyterpene and has an open carbon chain. The hexane formula does not really represent an oxypolyterpene, but a condensation product of a terpene alcohol of the type of an ether. The complex molecule of gutta-percha or caoutchouc is doubtless split up on oxidation, but there is no evidence to show that the disintegration is as thorough as Tschirch's formula would imply.

The nature of the products formed by the oxidation of gutta-percha and caoutchouc by air may be conveniently studied by examining the resin of pontianac (Dead Borneo, Besk), which can be readily obtained and at little cost. Pontianac consists of about 70 per cent. of resin and 30 of caoutchouc; the resin has been proved to stand in the same relationship to the caoutchouc substance as the resin of gutta-percha to

gutta-percha itself. A *compound*, $C_{50}H_{80}O_2$, isolated from the mixture of pontianac resins, melts at 161°, and when dissolved in chloroform gives the same reaction with sulphuric acid as spherite alban.

E. W. W.

Colophony. WILHELM FAHRION (*Zeit. angew. Chem.*, 1904, **17**, 239—241. Compare Abstr., 1902, i, 165).—The author maintains that his autoxidation theory with respect to colophony is correct.

A. McK.

A Copal Resin and a New Kino yielded by the Fruit and Bark respectively of Dipteryx Odorata. EDOUARD HECKEL and FREDÈRIC SCHLAGDENHAUFFEN (*Compt. rend.*, 1904, **138**, 430—432).—A new kino or tanno-glucose was obtained during September by oblique incision of the bark of *Dipteryx odorata* in French Guiana. The trees were fifteen years of age and fully grown. The product is reddish-brown in colour, but transparent; it is slightly soluble in water and possesses a bitter taste. Ferric chloride and ammonia produce a violet colour in the aqueous solutions, the latter are also coloured violet by boiling with finely-divided iron; the addition of acids changes the violet to a red coloration. Aqueous solutions of the kino reduce potassium ferricyanide to the ferrocyanide. When the resin is heated in the dry state, catechol is formed. The ash after ignition forms 0·15 per cent. of the whole; it contains iron, manganese, and calcium.

S. S.

Caricari Elemi. ALEXANDER TSCHIRCH and L. REUTTER (*Arch. Pharm.*, 1904, **242**, 117—121. Compare Abstr., 1902, i, 812; 1903, i, 430).—The sample examined was exhibited as "caricari" at the Brazilian Exhibition of 1886 in Berlin; it had an acid number 27 and saponification number 59. From the solution in ether, 1 per cent. aqueous ammonium carbonate extracted iso*carieleminic acid*, $C_{38}H_{56}O_4$; this melts at 75—76°, and is monobasic, with the acid number 90. From the mother liquor, one per cent. aqueous sodium carbonate then extracts two acids; from a solution of these in ether-alcohol *carielemic acid*, $C_{38}H_{56}O_4$, crystallises; this melts at 215°, and is monobasic, with acid number 94. The amorphous *carielemic acid*, $C_{37}H_{56}O_4$, remains in solution; this melts at 120° and is monobasic, with acid number 87.

The residual solution, after distillation of the ether, yielded a volatile *essential oil* on distillation with steam; a *bitter-substance* was also present. The residue was dissolved in ether-alcohol; crystals separated having the composition $C_{30}H_{50}O$ and $D([\alpha]_D?) + 90°35'$. These, when benzoylated, yielded the benzoates of α-amyrin and β-amyrin. The substance remaining in the ether-alcohol solution was *carieleresen*, $C_{24}H_{46}O_2$; it melts at 75—76°.

In 100 parts of the drug were found: *iso*carieleminic acid, 5; carieleminic acid, 12; carielemic acid, 20; essential oil, 3; amyrins, 3; carieleresen, 40; bitter-substance, impurities, loss, &c., 17 parts.

C. F. B.

Mastic. Alexander-Tschirch and L. Reutter (*Arch. Pharm.*, 1904, 242, 104—110).—The sample examined came from Chios; it had acid number 59 and saponification number 82·5. From the ethereal solution, 1 per cent. aqueous ammonium carbonate extracted the isomeric α- and *β-masticic acids*, $C_{23}H_{36}O_4$, which were separated by means of the respective insolubility and solubility of their lead salts in alcohol; they are amorphous, and monobasic with acid numbers 141 and 132 respectively; they melt at 90—91° and 89·5—90·5°.

One per cent. aqueous sodium carbonate then extracts a mixture of acids; that portion of the mixture which forms lead salts insoluble in alcohol was dissolved in alcohol, from which *masticolic acid*, also $C_{23}H_{36}O_4$, crystallised out; this melts at 201°, and is monobasic, with acid number 132; its *silver* salt was analysed. In the alcohol, amorphous *α-masticonic acid*, $C_{32}H_{48}O_4$, remained dissolved; this melts at 96—96·5°, and is monobasic, with acid number 107. Isomeric with this is the acid of which the lead salt is soluble in alcohol, *β-masticonic acid*; it melts at 91—92°, and is monobasic, with acid number 104.

From the remaining ethereal solution, aqueous potassium hydroxide extracts nothing. After the ether had been distilled off, the residue was distilled with steam, when an *essential oil* came over, and a resen remained; a *bitter-substance* is also present. Part of the resen, *α-masticoresen*, $C_{35}H_{56}O_4$, is soluble in alcohol; this part is amorphous and melts at 74—75°. The part insoluble in alcohol, *β-masticoresen*, is gummy in consistency.

In 100 parts of the drug were found: α- and β-masticic acids, 4; masticolic acid, 0·5; masticonic acid: α, 20; β, 18; masticoresens: α, 30; β, 20; essential oil, 2; bitter-substance, impurities, &c., 5·5 parts.

C. F. B.

Theory of Dyeing. Arthur Binz and Georg Schroeter (*Ber.*, 1904, 37, 727—730).—A reply to von Georgievics (this vol., i, 81).

W. A. D.

Brazilin and Hæmatoxylin. Josef Herzig and Jacques Pollak (*Ber.*, 1904, 37, 631—633. Compare Abstr., 1901, i, 478; 1902, i, 482; Kostanecki and Lloyd, Abstr., 1903, i, 645).—[With Galitzenstein.]—Cold concentrated sulphuric acid converts trimethylbrazilone into an *isomeride*, which forms white crystals, melts at 170—173°, and by prolonged boiling with acetic anhydride is converted into β-acetyltrimethyldehydrobrazilin. Alcohol and sulphuric acid convert it into β-trimethyldehydrobrazilin.

[With R. Fischer.]—Tetramethylhæmatoxylone reacts in quite similar manner, forming a crystalline *isomeride* which melts at 165—167° and yields β-acetyltetramethyldehydrohæmatoxylin on acetylation. The constitution of the two new compounds is in process of investigation.

C. H. D.

Nile-blue Base. Leonor Michaelis (*Pflüger's Archiv*, 1904, 101, 183—190).—A reply to Heidenhain (this vol., i, 179). The conclusion

of Heidenhain that proteids behave like acids towards Nile-blue base and that the change in colour, which proteids cause the base to assume, is due to salt-formation, is incorrect. Nile-blue base in dilute alcoholic solution is blue, whilst in concentrated alcoholic solution it is red; the blue coloration is not due to the action of atmospheric carbon dioxide. The reaction between cellulose and Nile-blue base does not necessarily indicate that salt-formation takes place. A. McK.

Synthesis of Furan Derivatives from Chloroacetaldehyde. GIUSEPPE PLANCHER and S. ALBINI (*Atti R. Accad. Lincei*, 1904, [v], 13, 39—43).—*Ethyl chloroethylideneacetoacetate*,

$$CO_2Et{\cdot}CAc{:}CH{\cdot}CH_2Cl,$$

prepared by saturating with hydrogen chloride a cold mixture of ethyl acetoacetate and chloroacetaldehyde hydrate, boils at 105—130° under 19—20 mm. pressure; when heated with alcoholic ammonia at 150° for 4 hours, it gives *ethyl 2-methylfuran-3-carboxylate*,

$$O<\begin{matrix}CMe{:}C{\cdot}CO_2Et\\ \quad\ \ |\\ CH{=}CH\end{matrix},$$

as an oil which, by hydrolysis, is converted into *2-methylfuran-3-carboxylic acid*, crystallising from water and melting at 102—103°.

From these facts, the authors conclude that in the formation of furan or pyrrole derivatives in Hantzsch's synthesis an ethylidene derivative is first formed, thus:

$$CO_2R{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}CO{\cdot}CH_2{\cdot}Cl \longrightarrow CH_3{\cdot}CO{\cdot}C(CO_2R){:}CMe{\cdot}CH_2{\cdot}Cl$$

$$\longrightarrow O<\begin{matrix}CMe{:}C{\cdot}CO_2R\\ \quad\ \ |\\ CH{=}CMe\end{matrix}$$

Action of Organo-magnesium Compounds on Lactones. I. JOSEF HOUBEN (*Ber.*, 1904, 37, 489—502).—The author has studied the application of the Grignard reaction to coumarin, the haloids used being methyl iodide, ethyl iodide, *iso*propyl bromide, bromobenzene, benzyl chloride, and α-naphthyl bromide.

2 : 2-Dimethyl-1 : 2-chromen, $C_6H_4<\begin{matrix}O{-}CMe_2\\ \quad\ |\\ CH{:}CH\end{matrix}$, formed by the action of magnesium methyl iodide on coumarin, is a clear liquid, which boils at 95—96° under 13·5 mm. pressure. It is neutral towards litmus and its solution in concentrated sulphuric acid is purple. Its formation is represented thus:

$$C_6H_4<\begin{matrix}O{-}CO\\ \quad\ |\\ CH{\cdot}CH\end{matrix} + MeMgI = C_6H_4(OMgI){\cdot}CH{:}CH{\cdot}COMe:$$

$$C_6H_4(OMgI){\cdot}CH{:}CH{\cdot}COMe + MeMgI = C_6H_4(OMgI){\cdot}CH{:}CH{\cdot}C(OMgI)Me_2.$$

The latter intermediate compound, when acted on by water, most probably forms dimethyl-*o*-coumaryl alcohol, from which water is then eliminated, thus:

$$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CMe_2{\cdot}OH \longrightarrow C_6H_4<\begin{matrix}O{-}CMe_2\\ \quad\ |\\ CH{:}CH\end{matrix}.$$

2 : 2-*Diethyl*-1 : 2-*chromen*, formed in an analogous manner, is a colourless liquid, which boils at 126—127° under 15 mm. pressure. It gives a red coloration with concentrated sulphuric acid and turns brown under the influence of light.

By the action of magnesium *iso*propyl bromide on coumarin, an oil, boiling at 136—141° under 11 mm. pressure, was obtained; it was probably the di*iso*propylchromen contaminated with bromine.

The action of magnesium phenyl bromide on coumarin proceeds in a different manner, *diphenyl-o-coumaryl alcohol* (αα-diphenyl-*o*-hydroxycinnamyl alcohol), $OH\cdot C_6H_4\cdot CH:CH\cdot CPh_2\cdot OH$, being isolated; it separates from alcohol in crystals melting at 164—166°. It is practically insoluble in an aqueous solution of sodium hydroxide; a phenoxide which is soluble in water with difficulty is, however, actually produced. In virtue of the hydroxyl grouping in the side-chain, it forms carbonium salts (compare Baeyer and Villiger, Abstr., 1902, i, 380, 769). The halochromism of diphenyl-*o*-coumaryl alcohol is exhibited when its solution in sulphuric acid is shaken with ether; the aqueous acid layer assumes a rosy tint, whilst the ethereal solution is colourless or only faintly yellow. Diphenyl-*o*-coumaryl alcohol is not converted by concentrated sulphuric acid into diphenylchromen or phenylflavene.

Benzyl o-hydroxystyryl ketone, $OH\cdot C_6H_4\cdot CH:CH\cdot CO\cdot CH_2Ph$, is formed by interaction of molecular amounts of magnesium benzyl chloride and coumarin, where the latter reacts quantitatively in the enolic form; it is a yellow syrup and boils at 217—219° under 12 mm. pressure. It is soluble with difficulty in a cold aqueous solution of sodium hydroxide.

No definite product was isolated from coumarin and magnesium α-naphthyl bromide. A. McK.

Dihydroxycoumaranone. WLADYSLAW FEUERSTEIN and K. BRASS (*Ber.*, 1904, 37, 817—820).—Dihydroxycoumaranone melts at 229° (compare Nencki, Abstr., 1894, i, 85) and may be formulated as $C_6H_4(OH)_2{<}{}^{O}_{CO}{>}CH_2$ or $C_6H_2(OH)_2{<}{}^{\text{—O—}}_{C(OH)}{\geqslant}CH$. The former should yield a diacetyl, and the latter a triacetyl derivative. Analysis is insufficient to determine the number of acetyl groups introduced, and hydrolysis causes complete destruction of the dihydroxycoumaranone. The *acetyl* derivative crystallises from dilute alcohol or light petroleum in slender, almost colourless needles and melts at 106°. Chloroacetyl chloride forms *di-chloroacetoxycoumaranone*, $C_6H_2(O\cdot CO\cdot CH_2Cl)_2{<}{}^{O}_{CO}{>}CH_2$, crystallising from light petroleum in leaflets and melting at 168°. The composition is determined by an estimation of the chlorine, and proves that dihydroxycoumaranone does not react in the enolic form (compare 5-hydroxycoumaranone, Brühl and Friedländer, Abstr., 1897, i, 221).

Alcoholic hydrogen chloride converts dihydroxycoumaranone into a dark violet condensation product melting above 300°. No hydrazone, oxime, or methyl derivative could be prepared. C. H. D.

Products of Condensation of Dihydroxycoumaranone and Aldehydes. WLADYSLAW FEUERSTEIN and K. BRASS (*Ber.*, 1904, **37**, 821—827. Compare preceding abstract).—Dihydroxycoumaranone condenses with aldehydes to form unsaturated ketones,

$$C_6H_2(OH)_2{<}{}^{-O-}_{CO}{>}C{:}CHR$$

(compare Kesselkaul and Kostanecki, Abstr., 1896, i, 606; Friedländer and Rüdt, *ibid.*, i, 607; Friedländer and Löwy, Abstr., 1897, i, 32). *p*-Dimethylaminobenzaldehyde forms 1-*p*-dimethylaminobenzylidene-5 : 6 dihydroxycoumaranone, $C_{17}H_{15}O_4N$, crystallising from anisole in bluish-violet crystals and melting at 281°. The *diacetyl* derivative, $C_{21}H_{19}O_6N$, forms violet, glistening needles melting at 215°. 1-p-*Nitrobenzylidene*-5 : 6-*dihydroxycoumaranone*, $C_{15}H_9O_6N$, from *p*-nitrobenzaldehyde, forms golden-bronze needles and melts above 360°; its *diacetyl* derivative melts at 219°. The *m*-nitro-compound forms yellow needles and melts at 274°, and the o-*nitro*-compound forms slender, yellow needles, and melts at 278°. 1-m-*Nitro*-p-*dimethylaminobenzylidene*-5 : 6-*dihydroxycoumaranone*, $C_{17}H_{14}O_6N_2$, forms slender, red needles and melts above 250°, its *diacetyl* derivative forms yellowish-red crystals and melts at 212°. 1-o-*Chlorobenzylidene*-5 : 6 *dihydroxycoumaranone*, $C_{15}H_9O_4Cl$, crystallises from dilute alcohol in yellow needles or leaflets, the latter having a green lustre, and melts at 253°. 1-p-*Methylbenzylidene*-5 : 6-*dihydroxycoumaranone*, $C_{16}H_{12}O_4$. from *p*-tolualdehyde, forms greenish-yellow scales and melts at 276°. 1-p-*Methoxybenzylidene*-5 : 6-*dihydroxycoumaranone*, $C_{16}H_{12}O_5$, forms slender, golden-yellow needles and melts at 252°. Concentrated alkali hydroxides decompose it on warming, forming anisaldehyde. 1-*Cinnamylidene*-5 : 6-*dihydroxycoumaranone*, $C_{17}H_{12}O_4$, crystallises in yellow, glistening scales and melts at 236°, dilute sodium hydroxide dissolves it to a deep violet solution, concentrated alkali sets free cinnamaldehyde on warming. 1-p-*Nitrocinnamylidene*-5 : 6-*dihydroxycoumaranone*, $C_{17}H_{11}O_6N$, forms dark red leaflets with bluish-violet reflex and melts at about 265°. 1-p-*Dimethylaminocinnamylidene*-5 : 6-*dihydroxycoumaranone*, $C_{19}H_{17}O_6N$, forms small, dark violet crystals and melts at 262°; its ethereal solution is fluorescent. The *diacetyl* derivative forms small, dark red needles and melts at 206°.

All the compounds described possess marked dyeing properties, and their behaviour towards various mordants is recorded in the paper.

C. H. D.

New Dinaphthapyranic [Dinaphthaxanthyl] Phenols ROBERT FOSSE (*Compt. rend.*, 1904, **138**, 282—284).—The author has previously shown (compare this vol., i, 83) that the dinaphthaxanthonium salts condense with the sodium salts of phenol, β-naphthol, or guaiacol to form derivatives in which the dinaphthaxanthyl residue takes the para-position to the hydroxyl group of the phenol when possible or, failing that, the ortho-position. In the present paper, the condensation products of dinaphthaxanthonium salts with *o*-, *m*-, and *p*-cresols are described. p-*Hydroxy*-m-*tolyldinaphthaxanthen*,

$$OH\cdot C_6H_3Me\cdot CH{<}{}^{C_{10}H_6}_{C_{10}H_6}{>}O\ [CH : Me : OH = 1 : 3 : 4],$$

the *o*-cresol derivative, is a pale red, crystalline solid melting at 232—233°, insoluble in aqueous, but soluble in alcoholic alkali solutions; it forms an acetyl derivative, which melts at 240° and is hydrolysed on boiling with alcoholic alkali solutions. p-*Hydroxy*-o-*tolyldinaphthaxanthen* [CH : Me : OH = 1 : 2 : 4], the *m*-cresol derivative, melts at 215°, and is soluble in benzene and alcoholic alkali solutions, but insoluble in aqueous alkali solutions; it forms colourless, crystalline, molecular combinations with 1 molecular proportion of ethyl alcohol, acetone, or acetic acid, which are not dissociated at 110°. o-*Hydroxy*-m-*tolyldinaphthaxanthen* [CH : Me : OH = 1 : 3 : 6], the *p*-cresol derivative, melts at 249—250°, is soluble in alcoholic, but insoluble in aqueous alkali solutions; its *acetyl* derivative melts at 232—233°, and its *ethyl* ether melts at 240—241°, and is insoluble in cold alcoholic or aqueous alkali solutions. M. A. W.

Union of Dinaphthaxanthonium Salts with Tertiary Aromatic Amines. ROBERT FOSSE (*Compt. rend.*, 1904, 138, 575—577).—When dinaphthaxanthonium bromide is mixed with dimethylaniline, the hydrobromide of *dimethyl*-p-*aminophenyldinaphthaxanthen* is formed. The base, $NMe_2\cdot C_6H_4\cdot CH{<}{\scriptstyle C_{10}H_6 \atop C_{10}H_6}{>}O$, is a white, crystalline solid, which melts at 207—208°, and is soluble in benzene, chloroform, or acetic acid. *Diethyl*-p-*aminophenyldinaphthaxanthen*, obtained in similar manner, melts at 230—231°. A proof of the constitution of these substances is afforded by the fact that they are also produced from the corresponding aminoaldehyde and *β*-naphthol; for example, the dimethyl derivative is formed by the action of dimethyl-*p*-aminobenzaldehyde (1 molecule) on *β*-naphthol (2 molecules) in presence of acetic anhydride and strong sulphuric acid. S. S.

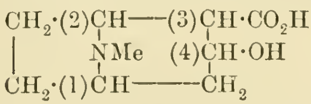
Liebermann's Thiophen Reaction. CARL SCHWALBE (*Ber.*, 1904, 37, 324—325).—Several samples of commercial "pure" benzene which were known to contain thiophen failed to respond to Liebermann's test, giving only a dirty brown, instead of the ordinary dark blue, coloration. Formerly all samples of benzene prepared from the coal tar of gas works responded to the test, but it is probable that the modern German method of obtaining benzene as one of the products of coke manufacture gives rise to a new impurity in the benzene which masks the reaction. W. A. D.

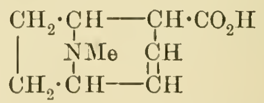
Optical Function of the Asymmetric Carbon Atoms in Ecgonine. JOHANNES GADAMER and T. AMENOMIYA (*Arch. Pharm.*, 1904, 242, 1—16).—Einhorn and Marquardt's conclusion that the anhydroecgonine obtained from *d*-*ψ*-ecgonine is identical with that from *l*-ecgonine (Abstr., 1890, 646) is confirmed by a comparison of the optical activity of the two products. Moreover, when anhydroecgonine is heated on the water-bath with 33 per cent. aqueous potassium hydroxide, a treatment which converts *l*-ecgonine into *d*-*ψ*-ecgonine, its optical rotation is unchanged; evidently that asymmetric carbon system which in *l*-ecgonine undergoes inversion can no longer be present in anhydroecgonine.

Hydroecgonine was prepared by reducing anhydroecgonine with sodium in boiling amyl-alcoholic solution (Willstätter, Abstr., 1897, i, 384). The aurichloride was not obtained with $3H_2O$, but with $5H_2O$, melting at 227°, and also anhydrous, melting at 233°. The hydrochloride was found not to be inactive, but to have a slight lævorotation; this is shown not to be due to an admixture of anhydroecgonine, but it might be caused by a little *l*-ecgonine hydrochloride. When anhydroecgonine is boiled with amyl-alcoholic sodium amyloxide, its rotation is not changed; probably, therefore, its three asymmetric carbon systems persist unchanged in hydroecgonine.

Anhydroecgonine dibromide hydrobromide (Eichengrün and Einhorn, Abstr., 1891, 66) has $[\alpha]_D$ +30° in 3 per cent. solution. When an attempt was made to obtain a better yield by using only a gentle heat, a salt was obtained which melted at the same temperature, and also yielded a perbromide (dibromo-compound) melting at 145°; it crystallised with $4H_2O$, however, instead of $3H_2O$, and was lævorotatory with $[\alpha]_D$ −82° in 3 per cent. solution. Attempts to convert into hydroecgonine by the action of zinc and acetic acid or of zinc-palladium and concentrated hydrochloric acid were unsuccessful, anhydroecgonine being regenerated. Hydrobromoanhydroecgonine hydrobromide (*loc. cit.*, 94) has $[\alpha]_D$ +42° in 1 per cent. solution.

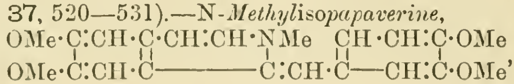
By a consideration of these results and those of other investigators, the conclusion is reached that anhydroecgonine has the formula appended, and that in *l*-ecgonine the asymmetric systems 1, 2, 3, 4 are respectively *l*, *d*, *l*, *l*, whilst in *d*-ψ-ecgonine 4 is *d*; the system 4 must cause a rotation of ±39° (compare Abstr., 1902 i, 174).


Ecgonine.


Anhydroecgonine.

C. F. B.

Papaverinium Bases. Herman Decker and Oskar Klauser (*Ber.*, 1904, 37, 520—531).—N-*Methyl*iso*papaverine*,



prepared by the action of sodium hydroxide on papaverine methiodide, forms transparent, yellow, hygroscopic, monoclinic crystals [$a:b:c$ = 0·8841 : 1 : 0·8188; β = 96°15′], and melts at 129—131°. Its aqueous solution reacts alkaline towards litmus, and reduces copper sulphate solution. The solution contains the quaternary papaverine hydroxide, from which the yellow base may be regenerated either by concentration of the aqueous solution or by the addition of sodium hydroxide. The *picrate* melts at 129—130°.

N-*Ethyl*iso*papaverine* melts at about 101°; its *picrate* melts at 154—155°. In aqueous solution of the base, the transformation into ethylpapaverinium hydroxide takes place.

N-*Benzyl*iso*papaverine*, prepared by the addition of sodium hydroxide solution to a solution of papaverine benzyl chloride, separates

from alcohol in golden-yellow scales and melts at 139—140°. In contradistinction to the bases just described, the equilibrium with the corresponding hydroxide is very slowly attained in aqueous solution. Its *picrate* melts at 192°.

When a current of air was passed through a 1 per cent. solution of *N*-benzyl*iso*papaverine to which sufficient sodium hydroxide solution had been added to cause a faint turbidity, an intense odour of methylvanillin was soon developed; the oxidation was complete after several days. The crystalline product which separated proved to be 6 : 7-*dimethoxy-2-benzyl*-1-iso*quinolone*, $C_9NH_4O(OMe)_2 \cdot C_7H_7$, which crystallises from alcohol in silky needles and melts at 167°. Its *picrate* melts at 133°.

Veratric acid was also obtained in small amount as a product of the oxidation of *N*-benzyl*iso*papaverine; its presence is due to the oxidation of the methylvanillin initially formed.

6 : 7-*Dihydroxy-2-benzyl*-1-iso*quinolone*, prepared by the removal of the methoxyl groups from the preceding dimethoxyquinolone, separates from xylene in lustrous, silvery scales and melts at 225°.

A. McK.

Ricinine. Léon Maquenne and Louis Philippe (*Compt. rend.* 1904, **138**, 506—508. Compare Tuson, Trans., 1864, **17**, 195; Schulze, Abstr,, 1898, i, 42; Evans, Abstr., 1900, i, 309).—The ricinine used in this investigation was obtained from the commercial cakes of ricin, and the yield amounted to about 0·2 per cent. Pure ricinine, $C_8H_8O_2N_2$, melts at 201·5° (corr.), and loses one mol. of methyl alcohol on saponification with potassium hydroxide, yielding ricininic acid, $C_7H_6O_2N_2$, which crystallises in slender, brilliant needles, decomposes at 320°, is almost insoluble in cold, but soluble in 100 parts of boiling water. Ricininic acid is readily decomposed by heating to 150° in a sealed tube with hydrochloric acid with the elimination of carbon dioxide and ammonia, and the formation of the hydrochloride of a hydroxymethylpyridone, $C_6H_7O_2N,HCl,2H_2O$, which melts at 65—70°, becomes anhydrous at 110°, and melts at 155—160°. Hydroxymethylpyridone, $C_6H_7O_2N$, separated from the latter salt by the action of silver oxide or ammonia, crystallises in colourless needles containing one molecular proportion of water of crystallisation, the hydrated compound melts at 80°; the anhydrous, which melts at 170—171°, is readily soluble in warm water or alcohol, and almost insoluble in ice-water; the molecular weight, as determined by the ebullioscopic method in alcohol, confirms the foregoing formula. Ricinine is therefore the methyl ester of an iminomethylpyridinecarboxylic acid, the following formulæ representing the probable constitution of the compound and its two degradation products:

$$N{<}\begin{matrix} C(CO_2Me) \cdot C \\ CMe{=}CH \cdot C \end{matrix}{>}NH \qquad N{<}\begin{matrix} C(CO_2H) \cdot C \\ CMe{:}CH \cdot C \end{matrix}{>}NH \qquad NH{<}\begin{matrix} CH{:}C(OH) \\ CMe{=}CH \end{matrix}{>}CO$$

Ricinine. Ricininic acid. Methyloxypyridone.

M. A. W.

Preparation of 8-Mono-, Di- and Tri-chloromethylxanthines. C. F. BOEHRINGER & SÖHNE (D.R.-P. 146714. Compare Abstr., 1902, i, 125, 504).—The homologues of xanthine described in the former patents and containing an 8-methyl group may be chlorinated by means of gaseous chlorine acting on a solution or suspension of the compound, or by sulphuryl chloride, phosphorus pentachloride, &c. One, two, or three hydrogen atoms of the methyl group may thus be replaced, yielding stable compounds which have no basic properties. 8-*Chloromethylcaffeine*, $C_9H_{11}O_2N_4Cl$, from 8-methylcaffeine, crystallises from alcohol or ethyl acetate in thick, white needles, melts at 208—210°, and dissolves readily in hot chloroform. 8-*Dichloromethylcaffeine*, $C_9H_{10}O_2N_4Cl_2$, crystallises from alcohol in colourless needles and melts at 230—232°. 8-*Trichloromethylcaffeine*, $C_9H_9O_2N_4Cl_3$, forms white needles melting at 182—184°. 8-*Trichloromethyltheobromine* (3 : 7-dimethyl-8-trichloromethylxanthine), from 8-methyltheobromine, crystallises from ethyl acetate in glistening prisms containing ethyl acetate, which they lose on exposure to air and then melt at 211—212°. C. H. D.

[8-Trichloromethyl-7-chloromethyl-1 : 3-dimethylxanthine.] C. F. BOEHRINGER & SÖHNE (D.R.-P. 146715. Compare preceding abstract).—By energetic chlorination of the homologues of 8-methylxanthine, as by the action of gaseous chlorine on a solution in nitrobenzene on the water-bath, the three hydrogen atoms of the 8-methyl group and also one hydrogen atom of the 7-methyl group may be replaced by chlorine. Thus, 8-methylcaffeine yields 8-*trichloromethyl-7-chloromethyl-1 : 3-dimethylxanthine*, $\begin{array}{l}NMe\cdot CO\cdot C\cdot N(CH_2Cl)\\ \vert \qquad\qquad \Vert \\ CO\cdot NMe\cdot C\text{———————}N\end{array}\!\!>C\cdot CCl_3$, crystallising from alcohol in large, colourless prisms and melting at 204—205°. C. H. D.

2-Methylpyrroline and 1 : 2-Dimethylpyrroline. LUIGI MASCARELLI and GIUSEPPE TESTONI (*Gazzetta*, 1903, 33, ii, 312—318).—The abnormal properties of Hielscher's 2-methylpyrroline and 1 : 2-dimethylpyrroline (Abstr., 1898, i, 338) is probably due to their containing the double linking between positions 2 and 3; their structures would then be $NH<\begin{array}{l}CMe{:}CH\\ CH_2\text{-}CH_2\end{array}$ and $NMe<\begin{array}{l}CMe{:}CH\\ CH_2\text{-}CH_2\end{array}$. They differ from the ordinary methylpyrrolines in being less stable in the air or on distillation, but are somewhat more resistant than these to potassium permanganate, although their stability in this respect is not sufficient to justify the assumption of a double linking between carbon and nitrogen. Attempts, however, to prove the existence of the :NH radicle in the 1-methylpyrroline by means of nitrous acid and by phenylcarbimide failed, but this is explained by the presence of the adjacent methyl radicle. By reduction with tin and hydrochloric acid, the 1-methylpyrroline is converted into 1-methylpyrrolidine; with methyl iodide, it forms a *methiodide*, $MeI,NH<\begin{array}{l}CMe{:}CH\\ CH_2\text{-}CH_2\end{array}$, which crystallises from absolute alcohol in large, rectangular plates, melts

and decomposes at 260°, and is converted by aqueous potassium hydroxide into Hielscher's 1 : 2-dimethylpyrroline.

On bromination in glacial acetic acid, the 1 : 2-dimethylpyrroline gives a *dibromo*-1 : 2-*dimethylpyrroline hydrobromide*, which crystallises from absolute alcohol in orange-yellow, striated leaflets melting at 125°. W. A. D.

Compounds of Metallic Thiocyanates with Organic Bases. HERMANN GROSSMANN (*Ber.*, 1904, 37, 559—569).—*Pyridine silver thiocyanate*, $AgSCN,C_5H_5N$, separates from solution in pyridine in decimetre-long (?), glistening, prismatic needles, which soon lose their lustre by exposure to air, liberate pyridine slowly at atmospheric temperatures, but completely at 110°.

Pyridine cuprous thiocyanate, $CuSCN,2C_5H_5N$, separates from pyridine in yellow, thin prisms, or stouter crystals of darker colour, and dissociates in the air.

Pyridine lead thiocyanate, $Pb(SCN)_2,2C_5H_5N$, crystallises from pyridine in well-formed, glistening, orthorhombic prisms of pale yellow colour, is more stable in the air than the silver and cuprous compounds, and is decomposed by water, yielding pyridine and a basic salt.

Manganese thiocyanate, $Mn(SCN)_2,3H_2O$, prepared by the action of manganese sulphate on barium thiocyanate, separates from the green, syrupy aqueous solution in large, green crystals which soon effloresce in the air. An excess of pyridine precipitates from an aqueous solution of the salt a *compound*, $Mn(SCN)_2,4C_5H_5N$, which crystallises from aqueous pyridine, alcohol, or anhydrous pyridine in glistening, colourless, monoclinic prisms, which show strong interference colours, but are not stable in the air. Manganous thiocyanate forms the *compound* $Mn(SCN)_2,2C_5H_5N$, which separates from an alcoholic solution in yellow, crystalline masses.

A *hexapyridine manganous bromide*, $MnBr_2,6C_5H_5N$, was prepared by crystallising manganous bromide from anhydrous pyridine; it separates in four-sided, glistening, pale-green, rhombohedral tablets and soon effloresces in the air.

Anhydrous nickel thiocyanate, $Ni(SCN)_2$, forms a dark chocolate-coloured, amorphous powder which, when covered with water, becomes yellow and finally yields a green solution.

The *compound*, $Ni(SCN)_2,4C_5H_5N$, is precipitated by an excess of pyridine from an aqueous solution of the thiocyanate as a blue, crystalline precipitate, and crystallises from water, alcohol, or pyridine in beautiful, glistening, clear-blue, monoclinic, prismatic needles.

Tetrapyridine cadmium thiocyanate, $Cd(SCN)_2,4C_5H_5N$, prepared by crystallising cadmium thiocyanate from pyridine, separates in long, glistening, colourless, monoclinic prisms, which lose pyridine on exposure to air. *Dipyridine cadmium thiocyanate*, $Cd(SCN)_2,2C_5H_5N$, prepared by the action of pyridine on a cold aqueous solution of cadmium thiocyanate, is precipitated in the form of heavy, white, microscopic needles. *Pyridinium cadmium thiocyanate*,

$$(C_5H_6N),Cd(SCN)_3,$$

prepared by dissolving cadmium thiocyanate in aqueous pyridine thio-

cyanate at 100°, forms colourless prisms. *Pyridinium cadmium chloride*, $(C_5H_6N)CdCl_3$, prepared by dissolving dipyridine cadmium chloride in aqueous hydrogen chloride, separates, on concentrating the solution, in long, colourless, monoclinic needles. *Pyridinium cadmium bromide*, $(C_5H_6N)CdBr_3$, prepared by a similar method, crystallises in hexagonal tablets.

Tetrapyridine zinc thiocyanate, $Zn(SCN)_2,4C_5H_5N$, prepared by crystallising zinc thiocyanate from pyridine, forms glistening, prismatic, monoclinic crystals. *Dipyridine zinc thiocyanate*, crystallises from alcohol in thin, prismatic, colourless, monoclinic needles. Water decomposes the zinc and cadmium compounds.

Pyridinium zinc bromide, $(C_5H_6N)_2ZnBr_4$, prepared by dissolving pyridine zinc bromide, $ZnBr_2,2C_5H_5N$, in hydrobromic acid, crystallises readily in soluble, colourless, stout, monoclinic prisms. *Pyridinium zinc thiocyanate*, $(C_5H_6N)Zn(SCN)_4$, separates in thin, monoclinic prisms. T. M. L.

Gold Salts of Pyridine Bases. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1903, 1082—1083).—The author points out that he has already described (Abstr., 1881, 56 and 288) gold salts of β-lutidine analogous to those of pyridine described by François (Abstr., 1903, i, 652). T. A. H.

Action of Formaldehyde on α-Picoline (2-Methylpyridine). ANDREAS LIPP and J. RICHARD (*Ber.*, 1904, 37, 737—746. Compare Koenigs and Happe, Abstr., 1903, i, 850).—*Dimethylol-2-picoline* [2-*αγ-dihydroxy*iso*propylpyridine*], $C_5NH_4\cdot CH(CH_2\cdot OH)_2$, is prepared with a good yield by heating 2-picoline with 40 per cent. formaldehyde for 20 hours at 130—140°; hydroxymethyl-2-picoline (2-picolylalkine) is probably first formed, as, when heated with formaldehyde under the given conditions, it is converted into the dimethyl derivative. When purified by means of its mercurichloride, it crystallises from absolute alcohol on adding anhydrous ether in colourless prisms or needles and melts at 78°. The *mercurichloride*, $C_8H_{11}O_2N,HCl,6HgCl_2$, forms white nodules and crystals and melts at 161—162°; the *platinichloride* melts at 138—139° and decomposes at 142°; the *aurichloride* melts at 123—124°; the picrate melts at 106·5—107·5° (Koenigs and Happe give 108—110°). The *dibenzoyl* derivative, $C_5NH_4\cdot CH(CH_2\cdot OBz)_2$, crystallises from ether in colourless plates or prisms and melts at 90—91°; its *platinichloride* melts at 112—114°. The *monoacetyl* derivative, $C_5NH_4\cdot CH(CH_2\cdot OH)\cdot CH_2\cdot OAc$, prepared by acetylation with acetyl chloride at the ordinary temperature, is a colourless oil which gives a crystalline *platinichloride*, $(C_{10}H_{13}O_3N)_2,H_2PtCl_6,H_2O$, melting at 155—157°. *Dimethylol-2-picoline methochloride*, although not obtained crystalline, gives well-characterised salts; the *mercurichloride*, $C_9H_{14}O_2NCl,6HgCl_2$, melts at 152—154°, the *platinichloride*, $(C_9H_{14}O_2N)_2PtCl_6,2H_2O$, after losing its water of crystallisation, melts at 142—145°, and the *aurichloride* at 97—98°. On oxidising dimethylol-2-picoline with aqueous potassium permanganate, picolinic acid is obtained, showing that both of the methylol groups are in the side-chain.

When dimethylol-2-picoline is distilled under reduced pressure, it loses water and is converted into *methylene-methylol-2-picoline*,

$$C_5NH_4\cdot C(CH_2\cdot OH):CH_2,$$

which boils at 135—140° under 10—12 mm. pressure and does not solidify at −20°. The following salts are crystalline; the *hydrochloride* melts at 131—132°, the *mercurichloride*,

$$C_8H_9NO,HCl,6HgCl_2,$$

at 176—177°, the *platinichloride* decomposes at 170°, and the *aurichloride* and *picrate* melt at 131° and 110—111° respectively. The *acetyl* derivative, $C_5H_4N\cdot C(CH_2\cdot OAc):CH_2$, is obtained on heating dimethylol-2-picoline with acetic anhydride, and boils at 140—144° under 13 mm. pressure; the *platinichloride* melts at 159—161°. The *dibromide*, $C_5NH_4\cdot CBr(CH_2Br)\cdot CH_2\cdot OAc$, of the acetyl derivative, prepared by adding bromine to its chloroform solution, crystallises from a mixture of alcohol and ether in lustrous prisms and melts at 89—90°. The *benzoyl* derivative, $C_5NH_4\cdot C(CH_2\cdot OBz):CH_2$, crystallises in tufts of prisms, melts at 60—61°, and is easily hydrolysed by boiling hydrochloric acid. W. A. D.

Indole Derivatives from Anethole. CARL HELL and H. COHÉN (*Ber.*, 1904, **37**, 866—872. Compare Möhlau, Abstr., 1883, 342; Fischer and Schmidt, *ibid.*, 1888, 698, 958; Bischler, *ibid.*, 1892, 1465; Collett, *Bull. Soc. chim.*, 1897, [iii], **17**, 66; Japp and Murray, Trans., 1894, 889; Hell and Günthert, Abstr., 1896, i, 20).—Anisyl bromomethyl ketone, obtained by Hell and Hollenberg's method (Abstr., 1896, i, 354), reacts with aniline in boiling alcoholic solution yielding small amounts of 2-*anisyl*-3-*methylindole*,

$$C_6H_4<{NH \atop CMe}>C\cdot C_6H_4\cdot OMe,$$

in the form of glistening plates melting at 123°. A better yield is obtained by working at 120°. 2-*Anisyl*-3 : 7-*dimethylindole* crystallises in colourless needles melting at 127°. 1-*Anisyl*-3 : 5-*dimethylindole* crystallises in glistening plates melting at 134°. α-Naphthylamine and anisyl bromoethyl ketone yield a product melting at 210°.

These indole derivatives do not yield acetyl derivatives (compare Bischler and Fireman, Abstr., 1893, i, 519), and on oxidation give anisic acid and a second acid melting at about 228°. J. J. S.

Indole Derivatives from Ethyl*iso*eugenol. CARL HELL and HERMANN BAUER (*Ber.*, 1904, **37**, 872—874).—Aniline and ethyl*iso*eugenole bromoethyl ketone (Hell and Portmann Abstr., 1896, i, 357) in alcoholic solution at 125° yield 2-iso*eugenyl*-3-*methylindole*, $C_6H_4<{NH \atop CMe}>C\cdot C_6H_3(OMe)\cdot OEt$, in the form of colourless plates melting at 165°. It yields an oily *nitrosoamine*, and a red, crystalline picrate. On oxidation, ethyl vanillic acid melting at 189° is obtained. *p*-Toluidine and the same ketone yield 2-iso*eugenol*-3 : 5-*dimethylindole* melting at 174°. J. J. S.

a a 2

Ammonium Compounds. XV. Synthesis of a Hydroxydihydro-base. HANS BÜNZLY and HERMAN DECKER (*Ber.*, 1904, 37, 575—577).—10-Methylacridone, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NMe}>C_6H_4$, reacts with magnesium phenyl bromide in the normal manner, and the product mixed with water yields hydroxyphenylmethyldihydroacridine, or, when acidified and treated with sodium bromide solution, yields phenylacridine methobromide (Abstr., 1903, i, 830). The *picrate* melts at 173°.

Acridine methiodide, $C_{14}H_{12}NI$, forms dark red needles and gradually loses methyl iodide.

10-*Methylacridinium picrate* melts at 191—192°. J. J. S.

Gallorubin. WLADYSLAW FEUERSTEIN and K. BRASS (*Ber.*, 1904, 37, 827—831).—Gallorubin (5 : 6-dihydroxyindirubin),

$$C_6H_2(OH)_2<\genfrac{}{}{0pt}{}{O}{CO}>C:C<\genfrac{}{}{0pt}{}{C_6H_4}{CO}>NH,$$

prepared by boiling dihydroxycoumaranone and isatin with hydrochloric acid, crystallises from alcohol in large, brownish-red, prismatic needles, containing 1 mol. alcohol. The compound melts at about 300°. after drying (compare Friedländer and Rüdt, Abstr., 1896, i, 607). Acetic anhydride and sulphuric acid convert it into *triacetylgallorubin*, $C_{22}H_{15}O_8N$, crystallising from a mixture of alcohol and chloroform in soft, orange needles and melting at 234°. Gallorubin combines with aniline to form *anilinodihydrogallorubin*,

$$C_6H_2(OH)_2<\genfrac{}{}{0pt}{}{O}{CO}>CH\cdot C(NHPh)<\genfrac{}{}{0pt}{}{C_6H_4}{CO}>NH,$$

crystallising from dilute alcohol in small, greenish-yellow leaflets, melting at 257°, and dissolving in alkali hydroxides to a greenish-yellow solution. C. H. D.

Basic Diphenylmethane and Triphenylmethane Dyes. JULIUS VON BRAUN (*Ber.*, 1904, 37, 633—646).—The question of the quinonoid structure of di- and tri-phenylmethane dyes may be tested by the preparation of derivatives such that the nitrogen of the amino-groups loses its power of becoming quinquevalent. This is effected by dialkylation and conversion into alkyl-cyano-compounds by the action of cyanogen bromide.

[With E. RÖVER.]—By the gradual addition of cyanogen bromide to partially fused tetramethyldiaminotriphenylmethane, *dicyanodimethyldiaminotriphenylmethane*, $CHPh(C_6H_4\cdot NMe\cdot CN)_2$, is produced, and separates from alcohol as a white, glistening powder, which melts at 163°, dissolves readily in benzene or chloroform, but is insoluble in water or acids. Concentrated sulphuric acid produces a slight yellow coloration, which is less the purer the cyanide is. Hydrogen sulphide forms the corresponding *thiocarbamide*, $CHPh(C_6H_4\cdot NMe\cdot CS\cdot NH_2)_2$, which melts at 200° and is insoluble in organic solvents. Boiling hydrochloric acid hydrolyses the cyanide, forming *dimethyldiaminotriphenylmethane*, $CHPh(C_6H_4\cdot NHMe)_2$, an uncrystallisable base, which may be distilled in steam and melts at 104°; the *picrate* forms

green needles and melts at 150°. Sodium nitrite forms the *nitrosoamine*, a dark yellow, crystalline powder, melting and decomposing at 149°. Phenylthiocarbimide yields the *phenylthiocarbamide*, $CHPh(C_6H_4 \cdot NMe \cdot CS \cdot NHPh)_2$, which forms white crystals melting at 124°.

Potassium permanganate in acetone solution oxidises the cyanide to *dicyanodimethyldiaminotriphenylcarbinol*, $OH \cdot CPh(C_6H_4 \cdot NMe \cdot CN)_2$, separating from alcohol or acetone as a white, crystalline powder and melting at 168°. It is insoluble in dilute acids, but dissolves in concentrated acids to intensely coloured solutions, from which it is precipitated unaltered by water. Salts with acids could not be isolated. Phenol condenses with it, forming the compound

$$OH \cdot C_6H_4 \cdot CPh(C_6H_4 \cdot NMe \cdot CN)_2,$$

which melts at 205°. No ether could be obtained by the action of alcohol on the carbinol. On boiling, acids hydrolyse it to *dimethyldiaminotriphenylcarbinol*, $OH \cdot CPh(C_6H_4 \cdot NHMe)_2$, melting at about 95°, and resembling the cyano-compound in its behaviour towards acids. The *zincochloride*, $(C_{21}H_{21}N_2Cl)_2,ZnCl_2,H_2O$, separates from hot water in dark green crystals and melts at 120°. The *nitrosoamine* melts and decomposes at 159°, the *phenylthiocarbamide* melts at 136°, both compounds behave in respect to acids like the carbinol.

The compounds $OH \cdot CPh(C_6H_4 \cdot NRR')_2$, in which R' = CN, NO, or CS·NHPh, and in which the nitrogen is no longer basic, are thus very weak bases in comparison with the tetra-alkylated carbinols. It is therefore concluded that they are true carbinol salts, in which the acid group is attached to methane carbon, whilst the salts of malachite-green, &c., possess the generally accepted quinonoid constitution, possibly taking up a second group, attached to the carbon atom, in presence of a large excess of concentrated acid, when the colour changes from green to red. C. H. D.

Electrochemical Reduction of Nitro-compounds of the Naphthalene, Anthracene, and Phenanthrene Series. JOHANNES MÖLLER (*Chem. Centr.*, 1904, i, 461—462; from *Elektrochem. Zeit.*, 10, 199—202, 222—226. Compare Abstr., 1901, i, 598, 646).—The nitro-compounds were dissolved in acid, a mixture of glacial acetic acid and sulphuric acid being usually employed. The current passed from a platinum anode in a porous cell to a cylindrical lead cathode of Tafel's pattern. By the reduction of 1 : 5- and 1 : 8-dinitronaphthalenes, 1 : 5- and 1 : 8-diaminonaphthalenes were formed respectively, but attempts to prepare nitronaphthylamines and tetrahydrodiaminonaphthalenes failed. 1 : 5-Dinitroanthraquinone, 2-nitrophenanthraquinone, and 2 : 7-dinitrophenanthraquinone, when reduced under similar conditions, yielded 1 : 5-diaminoanthraquinone, 2-aminophenanthraquinone, and 2 : 7-diaminophenanthraquinone respectively. Since attempts to isolate intermediate products failed in every case, a partial reduction of the nitro-groups cannot occur. The experiments also show that the carbonyl groups are not reduced.

A brief description of other experimental details is also given in the abstract. E. W. W.

Some Derivatives of Tetramethyldiaminophenyloxanthranol. ALFRED GUYOT and STŒHLING (*Compt. rend.*, 1904, 138, 211—213. Compare Haller and Guyot, Abstr., 1901, i, 350; 1903, i, 200, 348; this vol., i, 83).—Tetramethyldiaminophenyloxanthranol condenses readily with anisole to form a white, crystalline product melting at 176°, which is very soluble in benzene, and less so in alcohol or ether; it gives a white, crystalline condensation product with hydroxylamine melting at 203°, soluble in benzene and cold alcohol, and a yellow, crystalline condensation product with phenylhydrazine melting at 213°, soluble in benzene, and less so in alcohol. The formulæ ascribed to these compounds are: $C_6H_4{<}{\begin{matrix}C(OH)(C_6H_4\cdot NMe_2)\\C(OH)(C_6H_4\cdot OMe)\end{matrix}}{>}C_6H_3\cdot NMe_2$;

$$OH\cdot N{<}{\begin{matrix}C_6H_4{<}\begin{matrix}C(C_6H_4\cdot NMe_2)\\C(C_6H_4\cdot OMe)\end{matrix}{>}C_6H_3\cdot NMe_2\end{matrix}}, \text{ and}$$

$$NHPh\cdot N{<}{\begin{matrix}C_6H_4{<}\begin{matrix}C(C_6H_4\cdot NMe_2)\\C(C_6H_4\cdot OMe)\end{matrix}{>}C_6H_3\cdot NMe_2\end{matrix}},$$

respectively.

The following similar series of compounds were obtained by condensing tetramethyldiaminophenyloxanthranol and phenetole: (1) a crystalline, reddish-brown zincochloride melting at 199°, (2) a white, crystalline base, $C_{32}H_{34}O_3N_2$, melting at 175°, (3) a white, crystalline condensation product with hydroxylamine melting at 208°, (4) a yellow, crystalline condensation product with phenylhydrazine melting at 186°. M. A. W.

[Preparation of Aromatic Carbamides.] KALLE & Co. (D.R.-P. 146914. Compare Abstr., 1903, i, 555).—m-*Tolylenecarbamide*,

$$\left[C_6H_3Me{<}{\begin{matrix}NH\\NH\end{matrix}}{>}CO\right],$$

prepared by passing phosgene gas into a solution of *m*-tolylenediamine and sodium acetate so long as a precipitate is formed, is a white, crystalline powder, insoluble in ordinary solvents or in dilute acids or alkalis, and melts above 300°.

m-*Phenylenecarbamide* is a greyish-white, crystalline powder, insoluble in dilute acids or alkalis; 1 : 3-*naphthylenecarbamide*-6-*sulphonic acid* dissolves in warm water or in alkalis. C. H. D.

Monobenzoyl Derivatives of the Two Dibenzylhydrazines. G. EBERHARDT and ROBERT BEHREND (*Annalen*, 1903, 329, 363—366).—Behrens and Behrend (Abstr., 1902, i, 752) found, among the products of decomposition of bisnitrosylbenzyl, a substance, $C_{21}H_{20}ON_2$, having the composition of a monobenzoyldibenzylhydrazine, and melting at 168—169°.

The *monobenzoyl* derivative of *sym*-dibenzylhydrazine,

$$C_7H_7\cdot NBz\cdot NH\cdot C_7H_7,$$

could not be prepared by partially hydrolysing the dibenzoyl derivative, but was obtained by suspending the pure hydrochloride in ether or benzene, and adding the calculated quantities of sodium carbonate (calcined) and benzoyl chloride, and then boiling for a short time; the compound crystallises in plates or prisms melting at 85—87°, that is,

at the same temperature as β-benzoyl-β-benzyl-α-benzylidenehydrazine, which Curtius (Abstr., 1902, i, 831) at first thought was a benzoyl derivative of *sym*-dibenzylhydrazine.

The monobenzoyl derivative of *as*-dibenzylhydrazine,

$$N(C_7H_7)_2\cdot NHBz,$$

prepared by treating an ethereal solution of the base with dry potassium carbonate and benzoyl chloride, proved to be identical with the substance obtained by Behrens (*loc. cit.*); both specimens crystallise from alcohol in two different forms, one probably belonging to the monoclinic, and the other to the rhombic system; this benzoyldibenzylhydrazine is not changed by prolonged heating with 15 per cent. alcoholic potassium hydroxide or with 33 per cent. sulphuric acid.

K. J. P. O.

o-Aminobenzoylhydrazide and its Derivatives. C. THODE (*J. pr. Chem.*, 1904, [ii], 69, 92—104).—*o*-Aminobenzoylhydrazide, $NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot NH_2$, prepared by the action of hydrazine hydrate on isatoic acid or methyl anthranilate in the presence of alcohol, crystallises in monoclinic prisms from alcohol or short needles from chloroform, melts at 123°, and is easily soluble in hot water and alcohol, but less readily in benzene and ether. The *hydrochloride*, $C_7H_9ON_3,2HCl$, forms an amorphous compound which can be crystallised from alcohol.

At 200°, *o*-aminobenzoylhydrazide loses ammonia, giving *benzo*iso*pyrazolone* [iso*indazolone*], $C_6H_4<\substack{NH\\CO}>NH$, which forms prisms, melts at 206°, and, when treated with copper sulphate solution, yields a copper compound, $(C_7H_5ON_2)_2Cu,CuSO_4$, in green needles. As benzo*iso*pyrazolone is not acted on by acetic anhydride, it is regarded as isomeric with the substance (hydrazinobenzoic anhydride) to which this constitution was assigned by E. Fischer (Abstr., 1880, 647); the structure $C_6H_4<\substack{-NH-\\C(OH)}\geqslant N$ is suggested for the latter.

o-Aminobenzoylhydrazide readily condenses with aldehydes and ketones. o-*Aminobenzoylbenzylidenehydrazide*,

$$NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot N:CHPh,$$

crystallises in colourless needles melting at 195°, very easily soluble in warm alcohol and benzene; it yields an *acetyl* derivative,

$$NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot N:CHPh,$$

which forms prismatic plates, melts and decomposes at 180°, and is sparingly soluble in alcohol and glacial acetic acid. *Di*iso*propylideneaminobenzoylhydrazide*, $CMe_2:N\cdot C_6H_4\cdot CO\cdot NH\cdot N:CMe_2$, or possibly $C_6H_4<\substack{NH\cdot CMe_2\\CO-N\cdot N:CMe_2}$, crystallises in prisms, melts at 244°, is sparingly soluble in acetone, but readily in benzene or alcohol. o-*Aminobenzoylphenylethylidenehydrazide*,

$$NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot N:CMePh,$$

forms prismatic plates, melts at 165°, is fairly readily soluble in benzene and alcohol. o-*Aminobenzoyldiphenylmethylenehydrazide*,

$$NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot N:CPh_2,$$

crystallises in needles, melts at 157°, and is readily soluble in acetone, benzene, or alcohol.

On warming with formic acid, *o*-aminobenzoylhydrazide yields a *methenyl* derivative or *3-amino-4-ketodihydroquinazoline*,

$$C_6H_4{<}{\begin{matrix}N{=}CH\\ CO\cdot \overset{|}{N}\cdot NH_2\end{matrix}},$$

which forms prismatic needles, melts at 204°, and is soluble in alcohol, but less readily so in glacial acetic acid, ether, or water; with benzaldehyde, this yields an anil, $C_6H_4{<}{\begin{matrix}N{=}CH\\ CO\cdot \overset{|}{N}\cdot N{:}CHPh\end{matrix}}$, which forms leaflets melting at 129°, soluble in alcohol, less readily so in water and benzene. The corresponding compound, formed with salicylaldehyde, forms aggregates of needles, melts at 205°, and is soluble in alcohol, sparingly so in water, light petroleum, benzene, or ether.

With formic acid, *o*-aminobenzphenylhydrazide similarly yields 3-*anilino*-4-*ketodihydroquinazoline*, which forms prisms, melts at 140°, and is soluble in alcohol or benzene, sparingly so in ether or hot water.

Whilst, with *o*-aminobenzoylhydrazide, nitrous acid produces Weddige and Finger's benzoylazoimide, $C_6H_4{<}{\begin{matrix}N{=}N\\ CO\cdot \overset{|}{N}H\end{matrix}}$ (Abstr., 1887, 667), it gives, with *o*-aminobenzoylphenylhydrazide, the nitroso-derivative, $NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot NPh\cdot NO$, which decomposes at 78° and cannot be crystallised. It is decomposed by hot alcohol, giving slender needles of a compound melting at 206°, and having the composition $C_{13}H_{12}ON_2$.

G. D. L.

Action of Ammonium Persulphate on Thiobenzamide. REINHOLD VON WALTHER (*J. pr. Chem.*, 1904, [ii], 69, 44—48).—Ammonium persulphate oxidises thiobenzamide energetically to 3 : 5-diphenyl-1 : 2 : 4-thiodiazole, $CPh{\lessgtr}{\begin{matrix}S\cdot N\\ N{-}{-}\end{matrix}}{>}CPh$, which forms white needles melting at 91°, identical with the "dibenzenylazosulphime" obtained by Hofmann and Gabriel (Abstr., 1892, 1109) by the action of iodine on thiobenzamide. The product dissolves in concentrated hydrochloric acid, but the hydrochloride is decomposed by water. The *mercurichloride* forms white needles, the *platinichloride*,

$$(C_{14}H_{10}N_2S)_2,H_2PtCl_6,$$

prepared in glacial acetic acid solution, forms microscopic orange needles. Both salts are readily hydrolysed by water. C. H. D.

Preparation of Benziminazoles from Dinitrodiphenylamines. REINHOLD VON WALTHER and A. KESSLER (*J. pr. Chem.*, 1904, [ii], 69, 40—42).—Alcoholic ammonium sulphide reduces 2 : 4-dinitrodiphenylamine to 4-nitro-2-aminodiphenylamine, which forms yellow needles melting at 131° and red needles melting at 119°, the latter containing water (compare Nietzki and Almenräder, Abstr., 1896, i, 164). Acetic anhydride converts it into the acetyl derivative, but prolonged boiling with acetic anhydride, or boiling the acetyl derivative with dilute hydrochloric acid, forms 5-*nitro*-1-*phenyl*-2-*methylbenziminazole*, $NO_2\cdot C_6H_3{<}{\begin{matrix}NPh\\ {-}{-}N\end{matrix}}{\geqslant}CMe$, crystallising from alcohol in white

prisms melting at 170°, and forming a characteristic *platinichloride* and *mercurichloride*. Alcoholic ammonium sulphide reduces the base to 5-*amino*-1-*phenyl*-2-*methylbenziminazole*, a brown powder melting at 145—146°. C. H. D.

Benziminazoles and Oxidation Products of Orthodiamines. OTTO FISCHER (*Ber.*, 1904, 37, 552—558).—When oxidised by means of ferric chloride, dimethyl-*o*-phenylenediamine, $C_6H_4(NHMe)_2$, is converted into the *hydrochloride*, $C_{16}H_{20}N_4Cl_2,2H_2O$, of an unstable brownish-yellow azonium base; the hydrochloride separates from alcohol in red flakes with a green lustre and loses hydrogen chloride as well as water when heated at 130°. The *nitrate*, $C_{16}H_{20}O_6N_6$, crystallises from water or dilute alcohol in beautiful, stout prisms with a green, metallic lustre. The *mercurichloride*, $C_{16}H_{19}N_4HgCl_3$, separates from alcohol in needles with a green, metallic lustre. Reduction of the hydrochloride with zinc-dust yields a green solution, whilst tin and hydrochloric acid give methylamine hydrochloride and the tin-salt of a *base*, $C_{15}H_{19}N_3$, which separates from ether in nodular, crystal-masses, gives flashes of light when crushed, melts at 118°, and yields a deep green solution when the hydrochloric acid solution is acted on by ferric chloride, platinic chloride, or dilute nitric acid. The hydrochloride and base probably have the formulæ

$$C_6H_4<\begin{matrix}NMe-\!-\\NMeCl\end{matrix}>C_6H_2<\begin{matrix}NMe\\NHMe,HCl\end{matrix}$$

and $C_6H_4<\begin{matrix}NMe-\!-\!-\\NMe(OH)\end{matrix}>C_6H_2<\begin{matrix}NMe\\NHMe\end{matrix}$.

6-*Chlorobenziminazole*, $C_6H_3Cl<\begin{matrix}NH\\N\end{matrix}>CH$, prepared by the action of formic acid on 4-chloro-*o*-phenylenediamine (m. p. 76°, not 72° as given by Laubenheimer), crystallises from a mixture of benzene and light petroleum in nodular aggregates of colourless needles and melts at 125°; it separates from hot water in minute, white needles, which melt at 85° when air-dried and at 125° after driving off water of crystallisation. 6-*Chloro*-1 : 3-*dimethylbenziminazole iodide*, $C_9H_{10}N_2ClI$, prepared by heating the preceding compound with methyl alcohol and methyl iodide at 120—130°, crystallises from alcohol in white tablets, and is converted by cold sodium hydroxide into 6-*chloro*-1 : 3-*dimethylbenziminazolol*, $C_6H_3Cl<\begin{matrix}NMe\\NMe\end{matrix}>CH\cdot OH$, which crystallises from dilute methyl alcohol in flat, white prisms, melts at 106°, and becomes violet-red on exposure to moist air; its *platinichloride*, $C_{14}H_{12}N_2Cl_6Pt$, separates from hot dilute hydrochloric acid in long, orange-yellow prisms; the aurichloride separates in minute, golden-yellow needles. 4-*Chlorodimethyl*-o-*phenylenediamine*, $C_6H_3Cl(NHMe)_2$, prepared by boiling chlorodimethylbenziminazolol or the iodide of chlorodimethylbenziminazole with aqueous potassium hydroxide, crystallises from light petroleum in radiating aggregates of prisms, or in long, stout columns, and melts at 61°. Oxidation with ferric chloride yields, as in the previous case, a *hydrochloride*, $C_{16}H_{19}N_4Cl_3,2H_2O$, which separates as a paste of crystal flakes with bronze-like lustre, and crystallises from dilute alcohol; the *platinichloride*, $C_{16}H_{19}N_4Cl_7Pt,H_2O$, forms prisms

with a green, metallic lustre; the *iodide* is sparingly soluble and the *nitrate* readily soluble; the *bromide*, $C_{16}H_{19}N_4ClBr_2,H_2O$, forms beautiful, green needles, somewhat sparingly soluble in water; the *picrate*, $C_{16}H_{17}N_4Cl,2C_6H_3O_7N_3$, separates from dilute alcohol in dark-coloured needles with a metallic lustre, sparingly soluble in water; the *base* forms unstable, orange-coloured flocks, the hydrochloride is formulated as a *monochloro-N-tetramethyltetraminoazoniumchloride*,

$$Cl\cdot C_6H_3<\begin{matrix}NMe—\\NMeCl\end{matrix}>C_6H_3<\begin{matrix}NMe\\NHMe,HCl\end{matrix}$$

T. M. L.

Quinquevalent Nitrogen. I. A New Case of Stereoisomerism. OSSIAN ASCHAN (*Zeit. physikal. Chem.*, 1903, 46, 293—322. Compare Abstr., 1899, i, 542).—The two substances prepared by the action (1) of trimethylene bromide on dipiperidylethane, (2) of ethylene bromide on trimethylene dipiperidide, are found to be stereoisomeric; they are of the type Na_2bcd, and may be represented as follows:

$$(1)\quad C_5H_{10}:\overset{Br}{\overset{|}{N}}<\begin{matrix}CH_2———CH_2\\CH_2\cdot CH_2\cdot CH_2\end{matrix}>\overset{Br}{\overset{|}{N}}:C_5H_{10}\ \text{and}$$

$$(2)\quad C_5H_{10}:\overset{Br}{\overset{|}{N}}<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\CH_2———CH_2\end{matrix}>\overset{Br}{\overset{|}{N}}:C_5H_{10}.$$

The concentrated aqueous solution of each of these dibromides is optically inactive. From the first isomeride, ethylenetrimethylenedipiperidylium bromide (m. p. above 300°), a dichloride, a di-iodide (m. p. 300° with decomposition), a platinichloride, and a mercuric chloride double salt ($C_{15}H_{30}N_2Cl_2,2HgCl_2$, long, colourless needles, m. p. 189°) have been prepared. From trimethylene-ethylenedipiperidylium bromide, which becomes darker above 300° without showing a definite melting point, a platinichloride, a di-iodide (m. p. 282°, with decomposition), and a mercuric chloride derivative (long, colourless needles, m. p. 192°) have been prepared. The solubility of trimethylene-ethylenedipiperidylium bromide in 75 per cent. alcohol is considerably greater than that of ethylenetrimethylenedipiperidylium bromide, and a similar remark applies to the relative solubility of the two di-iodides in water.

Attempts have been made with the aid of *d*-bromocamphorsulphonate to resolve these diammonium dibromides into active components, but without success. It appears, therefore, that the bromine atoms must lie in the same plane as the middle ring, and that the two piperidine rings lie in planes perpendicular to that of the middle ring. This is in harmony with van't Hoff's diagram representing the bonds of quinquevalent nitrogen, which, however, may be simplified by supposing the nitrogen atom at the centre of a tetrahedron, four of the bonds going to the corners of the tetrahedron, and the fifth to the centre of gravity of one of the tetrahedron faces.

J. C. P.

Preparation of Phenylurazole from α-Ethyl Phenylsemicarbazidecarboxylate. SALOMON F. ACREE (*Ber.*, 1904, 37, 618—625. Compare Abstr., 1903, i, 867).—Potassium hydroxide hydrolyses α-ethyl phenylsemicarbazidecarboxylate to *potassium phenylsemicarbazide-α-carboxylate*, $CO_2K\cdot NPh\cdot NH\cdot CO\cdot NH_2$, which is converted into *potassium phenylurazole* by heating at 150°. The *silver* salt in similar manner forms silver phenylurazole at 150°. *Potassium phenylthiosemicarbazide-α-carboxylate*, $C_8H_8O_2N_3SK,2H_2O$, forms *potassium 1-phenyl-3-thiourazole* at 150°. *Sodium 1-phenyl-4-methylthiosemicarbazide-α-carboxylate* forms *sodium 1-phenyl-4-methyltriazolyl-3-mercaptol* at 130°. The *silver* salt of the mercaptol is crystalline and anhydrous. C. H. D.

A New Formula for the Basic Triphenylmethane Dyes. GEORG VON GEORGIEVICS (*Zeit. Farb. Text. Chem.*, 1904, 3, 37—39).—In order to explain the progressive diminution in colour of the triaminotriphenyl dyes on adding mineral acids to their solutions, and the fact that to each of the three phenylamino-radicles a definite chromophoric effect is to be attributed (compare Formánek, this vol., ii, 106), the author assumes that the three amino-radicles are intimately connected to form a colour centre, as shown, for example, in the formulæ:

$$C\left\langle\begin{array}{l}C_6H_4\cdot NH_2\\ C_6H_4\cdot NH_2\\ C_6H_4\cdot NH_2Cl\end{array}\right.\qquad C\left\langle\begin{array}{l}C_6H_4\cdot NMe_2\\ C_6H_4\cdot NMe_2\\ C_6H_4\cdot NMe_2Cl\end{array}\right.\qquad CPh\left\langle\begin{array}{l}C_6H_4\cdot NMe_2\\ C_6H_4\cdot NMe_2Cl\end{array}\right.$$

Pararosaniline. Crystal-violet. Malachite-green.

On adding 1HCl to, for instance, crystal-violet, one of the linkings between the nitrogen atoms is broken to form the compound

$$HCl,NMe_2\cdot C_6H_4\cdot C\left\langle\begin{array}{l}C_6H_4\cdot NMe_2\\ C_6H_4\cdot NMe_2Cl\end{array}\right.,$$

which, in structure and in the character of its absorption spectrum, resembles dyes of the diaminotriphenylmethane group. With a large excess of hydrochloric acid, the salt, $CCl(C_6H_4\cdot NMe_2,HCl)_3$, is ultimately obtained, which contains no chromophore linkings, and is hence colourless. This theory offers also a simple explanation of the fact observed by Hantzsch, that of the polyacid salts derived from crystal-violet, those of the carbinol base are much less dissociated in aqueous solution than those of the colour base; from the latter, hydrogen chloride is split off in solution because of the tendency of the nitrogen atoms to saturate each other. W. A. D.

Azo-compounds. Reduction of Nitrobenzoic Acids and Acetals. PAUL FREUNDLER (*Compt. rend.*, 1904, 138, 289—291. Compare Abstr., 1903, i, 371; this vol., i, 121).—When the acetal of

o-nitrobenzaldehyde is reduced by zinc and sodium hydroxide in the presence of alcohol, the chief product is the *acetal* of o-*azobenzaldehyde*, $N_2[C_6H_4 \cdot CH(OMe)_2]_2$ which melts at 144° and gives a hydrazone melting at 115°, the yield is 63 per cent. of the theoretical; there are formed in addition 15 per cent. of a basic aldehyde not yet identified, 5 per cent. of anthranilic acid, and a compound, $C_{14}H_8O_2N_2$, previously obtained in the reduction of *o*-nitrobenzyl-alcohol. The acetal of *m*-nitrobenzaldehyde, when similarly reduced, yields 93 per cent. of the theoretical quantity of the *acetal* of m-*azobenzaldehyde*, which melts at 86°, the corresponding aldehyde melting at 150°. The acetal of *p*-nitrobenzaldehyde yields on reduction 83 per cent. of the theoretical quantity of the acetal of *p*-azobenzaldehyde together with a small quantity of resin analogous to that formed by the reduction of the corresponding aldehyde (compare Alway, Abstr., 1903, i, 201, 425, 706). *o*-Nitrobenzoic acid yields on reduction 62 per cent. of *o*-azobenzoic acid and 10 per cent. of anthranilic acid, whilst under the same conditions, *p*-nitrobenzoic acid yields only *p*-azobenzoic acid.

In the reduction of these two series of compounds, only the ortho-substituted derivatives have given any appreciable quantity of the corresponding amide, and the author suggests that this may be due to steric hindrance. M. A. W.

Diazotisation of Nitrobenzene. EUGEN BAMBERGER and ALEXANDER WETTER (*Ber.*, 1904, **37**, 629—630).—The *rôle* of the substances taking part in the process of "diazotisation" may be so far reversed that ammonia (in the form of its sodium derivative) may be made to react with nitrobenzene with the formation of normal sodium diazoxide: $C_6H_5 \cdot NO_2 + NH_2Na = C_6H_5 \cdot N_2 \cdot ONa + H_2O$. The yield is extremely small, but the diazoxide can be recognised by its reaction with phenols. A better result is obtained by mixing sodamide with nitrobenzene and β-naphthol at a low temperature, when a reaction takes place, and benzeneazo-β-naphthol may be isolated from the product. Formation of aniline and sodium nitrite takes place to a small extent, but that this is not the cause of the formation of the diazoxide is shown by the fact that no trace of dye is produced from aniline, sodium nitrite, and β-naphthol in absence of water. When a small quantity of sodamide is warmed with nitrobenzene, sodium *iso*-diazoxide is produced; larger quantities react violently with charring.

C. H. D.

Preparation of Benzeneazodiphenylamines from Aminoazobenzene. REINHOLD VON WALTHER and A. LEHMANN (*J. pr. Chem.*, 1904, [ii], **69**, 42—44).—2 : 4-Dinitrochlorobenzene and aminoazobenzene combine at 130° to form 4′-*benzeneazo*-2 : 4-*dinitrodiphenylamine*, $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot N \colon NPh$, separating from glacial acetic acid in orange-red crystals and melting at 175·5—176°. Aminoazobenzene and picryl chloride form 4′-*benzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*, $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_4 \cdot N \colon NPh$, crystallising from benzene or acetic acid in golden-yellow leaflets and melting at 176—177°.

C. H. D

Benzeneazodiphenylamine-*o*-carboxylic Acid and its Homologues. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 146950).—*o*-Chlorobenzoic acid reacts with aminoazobenzene in presence of metallic copper or copper salts (compare Abstr., 1903, i, 754), forming *benzeneazodiphenylamine*-o-*carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot N_2Ph,$$

crystallising from alcohol in yellow needles and melting at 221—222°, almost insoluble in hot water, more soluble in hot alcohol. *Toluene*-o-*azo*-o-*tolylphenylamine*-o-*carboxylic acid* crystallises from benzene in needles and melts at 217—218°; *toluene*-p-*azo*-p-*tolylphenylamine*-o-*carboxylic acid* melts at 226—227°. C. H. D.

[Azo-dyes from 4-Chloro-2-aminophenol.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 144618).—Warm concentrated sulphuric acid converts 4-chloro-2-aminophenol into a monosulphonic acid, which may be diazotised and combined with 1 : 8-aminonaphthol-3 : 6-(or 2 : 4-)-disulphonic acid, forming dyes which give blue lakes with copper salts. C. H. D.

Disazo-dye from Chloroaminosalicylic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 144475).—*p*-Chloro-*o*-aminosalicylic acid, prepared by reduction of the corresponding nitro-acid (Abstr., 1880, 392), forms a *diazonium* compound crystallising in yellow needles, which may be combined with α-naphthylamine-6- or -7-sulphonic acid or a mixture of these. The resulting compound may be again diazotised and combined with β-naphthol. The product is a greenish-black, metallic powder, which dissolves in water to a reddish-violet solution, and forms a soluble, indigo-blue sodium salt.

C. H. D.

Azo-dyes from Aminoalphylhydroxynaphthyltriazolesulphonic Acids. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 146375).—Aminoalphylhydroxynaphthyltriazolesulphonic acids having the general formula

$$OH\cdot C_{10}H_{5-x}(SO_3H)_x\colon N_3\cdot R\cdot NH_2,$$

where R is an alphyl residue, are prepared by combining nitrophenyldiazonium salts with naphthylaminesulphonic acids containing an α-sulpho-group, and having an unsubstituted ortho-position relatively to the amino-group. Thus, diazotised *p*-nitroaniline combines with α-naphthylamine-3 : 6 : 8-trisulphonic acid, and when the resulting *o*-aminoazo-compound is oxidised by sodium hypochlorite, reduced by iron and acetic acid, and heated with sodium hydroxide, *sodium hydrogen* p-*aminophenyl*-8-*hydroxynaphthyl*-1 : 2-*triazole*-3 : 6-*disulphonate*, $NH_2\cdot C_6H_4\cdot N{<}{\genfrac{}{}{0pt}{}{N}{N}}{>}C_{10}H_3(SO_3Na)_2\cdot OH$, is obtained, crystallising in greenish-yellow leaflets. Similar products are obtained from diazotised *m*-nitroaniline or nitrotoluidine and β-naphthylamine-5 : 7-(or 6 : 8-)-disulphonic acid. C. H. D.

Preparation of 2 : 6-Tetrazophenol-4-sulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148085).—The tetrazonium compounds of 2 : 6-diaminoalkyloxybenzene-4-

sulphonic acids readily exchange their alkyloxy-group for hydroxyl, even in acid solution. The course of the reaction may be followed by combining the diazotised compound with β-naphthol. A rapidly prepared solution of the corresponding tetrazonium derivative combines with β-naphthol to form a red azo-compound, whilst a solution which has been prepared for some time yields a characteristic bluish-black disazo-dye. A large excess of acid and a low temperature should be employed during diazotisation, in order to prevent combination of the tetrazonium compound with the unaltered acid. 2 : 6-*Dinitroanisole-4-sulphonic acid*, prepared by nitrating anisole-*p*-sulphonic acid, forms a *potassium* salt crystallising in flat, colourless needles, becoming yellow in the light. Reducing agents form the 2 : 6-*diamino-acid*, separating in colourless, sparingly soluble needles, from which 2 : 6-*tetrazophenol-4-sulphonic acid* may be obtained in the manner described.
C. H. D.

Diazoamino-compounds of Iminazoles and Purine Derivatives. RICHARD BURIAN (*Ber.*, 1904, 37, 696—707).—Substituted iminazoles of the type $\begin{matrix} R^1C\cdot NH \\ \| \\ R^2C{-}{-}N \end{matrix}\!\!>\!CR^3$, which still retain the imino-radicle, interact with diazobenzene salts to form coloured diazoamino-derivatives of the general formula $\begin{matrix} R^1C\cdot N(\cdot N\!:\!NAr) \\ \| \\ R^2C{-}{-}{-}{-}{-}{-}{-}{-}N \end{matrix}\!\!>\!CR^3$.

Iminazole-1-diazobenzenesulphonic acid, $C_3N_2H_3\cdot N\!:\!N\cdot C_6H_4\cdot SO_3H$, prepared by the action of diazobenzenesulphonic acid or of diazotised sulphanilic acid on an ice-cold dilute alkaline solution of iminazole, crystallises in golden spangles and begins to decompose at 240—250°. 2-*Methyliminazole-1-diazosulphonic acid*, obtained similarly from 2-methyliminazole, is a red, crystalline powder. 2-*Phenyl-1-tetrazodiphenyliminazole*, $C_{12}H_8(N\!:\!N\cdot C_3N_2H_2Ph)_2$, prepared from 2-phenyliminazole (2 mols.) and diazotised benzidine (1 mol.), forms a brownish-red, crystalline powder, which blackens at 260°. 2-*Thiol-4 : 5-diphenyl-1-tetrazodiphenyliminazole*, $C_{12}H_8(N\!:\!N\cdot C_3N_2Ph_2\cdot SH)_2$, obtained in the same way from 2-thiol-4 : 5-diphenyliminazole (2 mols.) and benzidine forms orange-coloured aggregates of microscopic needles which soften at 110° and melt and decompose at 120—122°.

Iminazole-4 : 5-dicarboxylic acids, when combined with diazobenzenesulphonic acid, evolve carbon dioxide, and are converted into derivatives of iminazolemonocarboxylic acid, but which of the carboxyl radicles is eliminated has not been ascertained. *Carboxyiminazole-1-diazobenzenesulphonic acid*, $(C_4H_3O_2N)N\cdot N\!:\!N\cdot C_6H_4\cdot SO_3H$, prepared from iminazole-4 : 5-dicarboxylic acid, forms yellow needles or a red, microcrystalline powder and blackens above 265°.

Carboxy-2-methyliminazole-1-diazobenzenesulphonic acid,

$$C_{11}H_{10}O_5N_4S,2H_2O,$$

obtained from 2-methyliminazole-4 : 5-dicarboxylic acid, forms feathery aggregates of needles and darkens at 120°.

Carboxy-2-phenyliminazole-1-diazobenzenesulphonic acid, $C_{16}H_{12}O_5N_4S$, forms brownish-red aggregates of microscopic needles.

Purine derivatives, in virtue of the iminazole ring that they contain, are capable of combining with diazo-salts in the same manner; that it is the imino-radicle in position 7 which enters into action is shown by the fact that combination only occurs in the case of those compounds in which the hydrogen atom in position 7 is intact. Theobromine (3 : 7-dimethylxanthine) and caffeine (1 : 3 : 7-trimethylxanthine), for instance, fail to combine with diazobenzenesulphonic acid.

2 : 6-*Dioxypurine-7-diazobenzenesulphonic acid*,

$$C_5H_3O_2N_4 \cdot N{:}N \cdot C_6H_4 \cdot SO_3H,$$

prepared from xanthine and diazobenzenesulphonic acid, crystallises from water in rosettes of yellow needles. 2 : 6-*Dioxy*-1 : 3-*dimethylpurine-7-diazobenzenesulphonic acid*, prepared from theophylline, forms lustrous, orange-red needles. The *compounds* from guanine, hypoxanthine, and adenine form yellowish-red, bright yellow, and brownish-red needles respectively.

It is suggested that the production of colour by the union of a diazo-salt with the purine bases should be used as a qualitative test for these substances. The test is, however, not universally applicable, as its sensitiveness is affected by the presence of impurities, notably of reducing agents. W. A. D.

The Group of Simplest Proteids (Protamines). ALBRECHT KOSSEL and HENRY D. DAKIN (*Zeit. physiol. Chem.*, 1904, 40, 565—571).—In previous work, aminovaleric acid has been obtained from clupein, tyrosine from cyclopterin, scatoleaminoacetic acid from cyclopterin, pyrrolidine-2-carboxylic acid from salmin, and serin ($C_3H_7O_2N$) from clupein. The present investigation shows that aminovaleric acid and serin are more widely found; thus salmin yields both in addition to arginine and pyrrolidine-2-carboxylic acid. The protamines of carp sperm are at least two in number (α- and β-cyprinin). On decomposition, they yield basic products, arginine, lysine, tyrosine in small amount, aminovaleric acid, but not histidine. α-Cyprinin does not yield tyrosine. W. D. H.

The so-called Metallic Derivatives of Proteids from the Point of View of Chemical Equilibrium. GINO GALEOTTI (*Zeit. physiol. Chem.*, 1904, 40, 492—549).—The author has examined a number of precipitates of albumins with metallic salts, more especially those of egg-albumin with copper sulphate and egg-albumin with silver nitrate, from the point of view of the phase rule. The conclusions drawn are: (1) the precipitates, *metal albuminates*, obtained are not true chemical compounds of fixed composition in the sense required by the valency theory, they are indefinite substances varying considerably in composition. (2) The precipitation processes are reversible, and as a rule the precipitate dissolves in excess of one or other of the constituents. (3) The composition of the precipitate depends on the composition of the liquid in contact with it, as required by the thermodynamical laws of chemical equilibrium.

A summary of previous work is also given. J. J. S.

Physical Changes in the Condition of Colloids. III. Non-reversible Precipitation of Albumin by Electrolytes. WOLFGANG PAULI (*Beitr. chem. Physiol. Path.*, 1903, 5, 27—55. Compare Abstr., 1902, ii, 388; 1903, i, 299).—In contrast to the behaviour of alkali salts, the effect produced on albumin by calcium, strontium, and barium salts is non-reversible. The behaviour of the alkaline earth salts is intermediate between that of the alkali salts and that of heavy metal salts, in which latter case the influence of the cathion is the only determining factor. The chlorides and acetates of calcium, strontium, and barium are effective in inducing precipitation of albumin only in much more concentrated solution than the corresponding salts of the alkali metals. On the other hand, precipitation is induced by comparatively dilute solutions of the thiocyanates, iodides, and bromides.

The influence of salts of the alkali metals on the precipitating power of alkaline earth salts has been studied in detail. This power is increasingly intensified by various anions in the order given: $C_2H_3O_2'$, Cl', NO_3', Br', I', CNS'. Similarly, the alkali cathions are arranged in the order: $Mg^{\cdot\cdot}$, $NH_4^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$.

A solution of albumin becomes acid on addition of an alkaline earth salt, and it can be shown that in acid solution the changes produced in albumin by alkali salts also are non-reversible. The precipitation by alkaline earth salts, however, takes place equally well in alkaline solution, and the parallelism between the precipitation by alkaline earth salts and by alkali salts in acid solution is due to the firmer attachment of an electropositive ion. J. C. P.

Artificial Change of Albumin into Globulin. LEOPOLD MOLL (*Beitr. chem. Physiol. Path.*, 1903, 4, 563).—By warming serum to 60°, alkali-albumin is formed and the globulin is increased at the expense of the albumin. By warming to 56°, there is also increase in the globulin, but no formation of alkali-albumin. By similarly warming a dilute alkaline solution of crystalline serum-albumin, it is in part converted into globulin, first pseudo-globulin and then euglobulin. Globulin contains less sulphur than albumin; this is also true for the artificial globulin. Hydroxyl ions are regarded as the cause of the change. Neutral salts, especially of ammonium, inhibit the transformation; sugar acts, to a slight extent, in the same way, but urea hastens it. W. D. H.

Percaglobulin, a Characteristic Proteid of the Ovary of the Perch. CARL TH. MÖRNER (*Zeit. physiol. Chem.*, 1904, 40, 429—464).—The name *percaglobulin* is given to a proteid which is characteristic of the perch (*Perca fluviatilis*). It is not found in the ova. Like edestin, it readily passes into an insoluble modification (*percaglobulan*). It differs from other known globulins by its astringent taste, its precipitability by dilute hydrochloric acid, its high percentage of sulphur, and the property it has of precipitating certain gluco-proteids and polysaccharides, being itself precipitated at the same time.

W. D. H.

Decomposition Products of Gelatin. Phoebus A. Levene (*Zeit. physiol. Chem.*, 1904, **41**, 8—14, 99—100. Compare Abstr., 1903, i, 301; this vol., ii, 188).—A further account of observations already published. W. D. H.

Neutral Soluble Silver Compounds of Gelatoses. Farbwerke vorm Meister, Lucius, & Brüning (D.R.-P. 146792 and 146793).—Solutions of gelatose, prepared by heating gluten with water, may be neutralised by the addition of sodium hydroxide, and converted into the soluble silver derivative by adding insoluble silver compounds, such as silver lactate or silver succinimide, in the state of fine powder. Silver nitrate may also be employed (compare D.R.-P. 141967), the neutralisation being performed after the addition of the silver salt. C. H. D.

Theoretical Study of the Dissociation of Oxyhæmoglobin. Effects of Concentration and Temperature. Victor Henri (*Compt. rend.*, 1904, **138**, 572—574).—Hüfner, when studying the equilibrium of the system: oxyhæmoglobin, hæmoglobin, and oxygen, assumed that one molecule of each of these substances enters into the reactions; the numbers which he obtained for K were not constant, but varied with the concentration of hæmoglobin. It is now shown that Hüfner's experimental data lead to a more constant value for K, if the reaction be represented as oxyhæmoglobin (1 molecule) $\rightleftarrows$ hæmoglobin (2 molecules) $+ O_2$. Evidence is also adduced to show that the reaction is highly influenced by variations in temperature. S. S.

Hæmin from Different Sources, Dehydrochlorohæmin and Hæmatin. William Küster (*Zeit. physiol. Chem.*, 1904, **40**, 391—422. Compare Abstr., 1902, i, 845).—Nencki and Sieber's hæmin (Abstr., 1885, **69**, 825; 1886, 374, 482; 1888, 971), Schalféeff's acetylhæmin (Abstr., 1885, 566; 1886, 165; Nencki and Zaleski, Abstr., 1900, i, 709; 1901, i, 434), Morner's β-hæmin, and Cloetta's and Rosenfeld's hæmin (Abstr., 1898, i, 542), all have the same composition, $C_{34}H_{33}O_4N_4ClFe$, and the simple name hæmin for all of them is suggested. The substances were all purified and obtained in a crystalline form. On treatment with cold aniline, they lose the elements of hydrogen chloride and yield, after extraction with dilute acetic acid and ether, an amorphous product, *dehydrochlorohæmin*, $C_{34}H_{32}O_4N_4Fe$, which can be converted into hæmin.

Hæmatin, the product obtained by the action of aqueous alkalis on hæmin, has the composition $C_{34}H_{34}O_5N_4Fe$, and appears to be hæmin in which the chlorine has been replaced by hydroxyl; but it cannot be transformed back into hæmin.

Dehydrochlorohæmin, when dissolved in alkali and precipitated by acid, appears to be transformed into an isomeride, *dehydrohæmatin*, since it is no longer capable of being converted into hæmin. Hæmatin hydrobromide (Abstr., 1894, i, 312) has the composition $C_{34}H_{33}O_3N_4BrFe$.

Hæmin, on treatment with alcohol and hydrogen chloride or sulphuric acid, appears to yield ethyl ethers, but nitrogen is removed at the same time. J. J. S.

Action of Boiling Aniline on Hæmin. WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1904, **40**, 423—428).—Boiling aniline reacts with acetylhæmin yielding two products, $C_{58}H_{52}O_4N_8Fe$ and $C_{82}H_{79}O_5N_{11}Fe$, probably formed according to the equations:

$$C_{34}H_{32}O_4N_4Fe + 4C_6H_5{\cdot}NH_2 = C_{58}H_{52}O_4N_8Fe + 8H \text{ and}$$
$$C_{34}H_{32}O_4N_4Fe + 8C_6H_5{\cdot}NH_2 + O = C_{82}H_{79}O_5N_{11}Fe + NH_3 + 6H$$
$$\text{or } C_{58}H_{52}O_4N_8Fe + 4C_6H_5{\cdot}NH_2 + H_2O = C_{82}H_{79}O_5N_{11}Fe + NH_3.$$

The two compounds may be separated by the aid of acetone, in which the product of lower molecular weight is insoluble.

Mörner's hæmin gives a product from which a substance,

$$C_{70}H_{65}O_5N_9Fe\ (?),$$

soluble in acetone, can be isolated. J. J. S.

State of Combination of the Purine Bases in Nucleic Acid. RICHARD BURIAN (*Ber.*, 1904, **37**, 708—712).—Nucleic acid, prepared either from herring's roe, calves' thymus, or yeast, does not form at once a coloured compound with an alkaline solution of diazobenzenesulphonic acid (compare this vol., i, 354). On previously hydrolysing the nucleic acid from yeast, however, with hydrochloric acid, it readily forms a red compound, the analysis of which shows it to be xanthinediazobenzenesulphonic acid. From the thymonucleic acid, in a similar manner, guaninediazobenzenesulphonic acid is obtained. The author concludes that these observations show that the purine bases of nucleic acid are probably combined with phosphoric acid through the nitrogen atom in position 7; for example, in the case of guanine, thus:

$$\begin{array}{l} \quad NH{\cdot}CO{\cdot}C{-\!\!-}N{\cdot}P\vdots \\ \quad\ | \qquad\quad\ \| \qquad | \\ NH_2{\cdot}C{=\!=}N{-}C{\cdot}N{:}CH \end{array}.$$

W. A. D.

Hæmase. OSCAR LOEW (*Pflüger's Archiv*, 1903, **100**, 332—334. Compare Abstr., 1903, i, 544).—Senter has suggested the name hæmase for the catalase he has found in blood, without any proof that it acts differently from the catalases of plants. The name blood-catalase is suggested to indicate that all such substances decompose hydrogen peroxide in a similar way. W. D. H.

Influence of Hydrogen Ions on Invertase from Aspergillus Niger. ARISTIDES KANITZ (*Pflüger's Archiv*, 1903, **100**, 547—550).—From Fernbach's results on the influence of the concentration of sulphuric, oxalic, tartaric, succinic, lactic, and acetic acids respectively on invertase from *Aspergillus niger*, the author calculates, by aid of the dissociation constants of the acids referred to, that the invertase reaches its optimum in solutions which are 1/8000 to 1/300*N* with reference to hydrogen ions. At the latter concentration, the effect of the enzyme is not impaired. A. McK.

Function of Peroxides in the Living Cell. VII. Chemical Nature of Oxydases. ROBERT CHODAT and ALEXIS BACH (*Ber.*, 1904, 37, 36—43. Compare Abstr., 1903, i, 219, 378).—The fresh sap of *Lathræa squamaria*, which contains an oxydase, was acted on by a current of air and a 1 per cent. solution of barium hydroxide added drop by drop; a precipitate was produced which contained barium, gave the titanium reaction for hydrogen peroxide when decomposed with dilute sulphuric acid, and gave a blue coloration with starch and potassium iodide; no such effect was produced by stale sap which had lost its oxydase and become inactive, and it is suggested that the oxydase is simply an easily oxidisable substance which is converted into a peroxide by atmospheric oxygen. These peroxides are also produced in the living cell, and under the microscope with starch-iodide solutions thin sections show a blue coloration in the interior of the cell; this does not occur when the oxydase is absent, as tested, for instance, with guaiacum tincture, but the latter, being a more sensitive test, persists longer than the iodide reaction. The author cannot therefore accept Asō's conclusion, that the iodide reaction is produced by substances different from the oxydases.

The oxydases in some respects resemble nitrous acid, and a remarkable agreement is observed in the absorption of atmospheric oxygen by mixtures of nitrous acid and pyrogallol, and by oxydases mixed with pyrogallol, the presence of the nitrous acid and of the oxydase causing a great increase in the rate of absorption. Nitrous acid is, however, not present, and the purest oxydases contain very little albumin; oxydases prepared from moulds contain gummy substances, whilst Spitzer's preparations contain nucleo-proteids, but the active agent is probably independent of these associated materials.

T. M. L.

Manganese Salts as Oxydases in the presence of a Colloid. AUGUSTE TRILLAT (*Compt. rend.*, 1904, 138, 274—277. Compare this vol., i, 274).—A colloidal alkaline solution of a manganese salt exhibits properties which are strictly analogous to those of an oxydase, that is, it oxidises by acting as a carrier of atmospheric oxygen (compare Bertrand, Abstr., 1897, ii, 493); such a solution is prepared by mixing a 3 per cent. solution of egg albumin with 0·02 gram of manganous chloride and a 0·1 per cent. solution of sodium or potassium carbonate, and has the following properties: (1) it rapidly oxidises from the surface downwards when exposed to the air, but without the formation of a precipitate; (2) it gives no colour reaction with guaiacum, until exposed to the air, when the blue colour rapidly develops (compare Gessard, Abstr., 1903, i, 590); (3) it oxidises quinol to quinone and pyrogallol to purpurogallol (compare Bertrand, Abstr., 1895, i, 386); (4) the fresh solution gives no coloration with tetramethyldiaminodiphenylmethane (absence of MnO_2), but the blue colour develops on exposure to the air (presence of MnO_2) and disappears on the addition of an oxidisable substance (reduction of MnO_2) (compare Abstr., 1903, ii, 512); (5) the oxidation of phenolic compounds by the solution is accompanied by an evolution of carbon dioxide (compare Bertrand, Abstr., 1895, i, 386); (6), the solutions lose their characteristic pro-

perties when heated to 105°. For example, fresh colloidal solutions of manganese in the presence of gallic acid absorbed 45, 38, and 47 volumes of oxygen respectively, whilst the oxygen absorbed by the same solutions, after boiling, were 0, 5, and 3 volumes respectively.

M. A. W.

Oxidation of Vanillin by the Oxydase of Mushrooms. R. LERAT (*Compt. rend. Soc. Biol.*, 1903, 55, 1325—1327).—Bourquelot observed the formation of a greyish-white, crystalline precipitate as the result of the action on vanillin of the oxydase obtained from various kinds of mushroom. The present research shows that this substance is identical with Tiemann's dehydrodivanillin. Morphine yields under similar conditions dehydromorphine (Bourquelot).

W. D. H.

Magnesium α-Naphthyl Bromide. SALOMON F. ACREE (*Ber.*, 1904, 37, 625—628).—α-Bromonaphthalene reacts readily with magnesium in presence of a trace of iodine or methyl iodide, forming crystalline *magnesium α-naphthyl bromide*, which is converted by carbon dioxide in ethereal solution into α-naphthoic acid, some naphthalene being also formed. Benzophenone and magnesium α-naphthyl bromide condense to form diphenyl-α-naphthylcarbinol, benzoyl chloride and magnesium α-naphthyl bromide form phenyl α-naphthyl ketone, but not phenyldi-α-naphthylcarbinol. Condensation also takes place with other ketones and aldehydes.

The foregoing carbinols dissolve in concentrated acids to intensely coloured solutions, from which water precipitates the original compound, this behaviour being probably due to the formation of quinonoid salts.

C. H. D.

Organic Chemistry.

Inflammation of Light Petroleum. GERHARD JUST (*Zeit. Elektrochem.*, 1904, 10, 202—204).—In washing woollen articles with light petroleum, the vapour frequently takes fire, usually when an article is being lifted out of the liquid. It has been shown by Richter that the inflammation is due to a spark discharge of a charge of electricity produced by the friction between the wool and the liquid, and that the fires are completely prevented by adding from 1/50 to 1/20 per cent. of magnesium oleate to the petroleum. The author shows that the effect of the addition is not due to any change in the dielectric constant of the light petroleum, but that it is due to an increase in its conductivity. A gold leaf electroscope is attached to an electrode dipping into light petroleum, another electrode dipping into the liquid being earthed; the electroscope under these conditions will retain a charge of electricity for several minutes. When a 1/20 per cent. solution of magnesium oleate is used, it is hardly possible to charge the electroscope at all.

Fires due to a similar cause have been observed in pouring ether into glass bottles. T. E.

Oxidising Action of Ozone. CARL D. HARRIES (*Ber.*, 1904, 37, 839—841. Compare Abstr., 1903, i, 605, 807, 815; this vol., i, 15).—The nature of the reaction between ozone and unsaturated compounds depends on the presence or absence of water. In the absence of a solvent or in non-dissociating solvents, ozone is added at the double linking, forming *ozonides*,

$$>C{:}C< + O_3 = >\underset{O\cdot O\cdot O}{C\text{—}C}< \text{ or } O{<}\begin{matrix} O\cdot C{:} \\ O\cdot C{:} \end{matrix}.$$

In the presence of water, these ozonides are decomposed, forming ketones or aldehydes and hydrogen peroxide. It is possible that a small quantity of water may be sufficient to cause this decomposition, catalytic action taking place.

The ozonides are mostly highly explosive, but in some cases may be distilled under reduced pressure without decomposition. C. H. D.

$\beta\zeta$-Dimethyl-$\Delta^{\beta:\epsilon}$-heptadiene Diozonide. CARL D. HARRIES and RICHARD WEIL (*Ber.*, 1904, 37, 845—850).—Methylheptanone reacts with magnesium methyl iodide, forming *ζ-hydroxy-$\beta\zeta$-dimethyl-Δ^{β}-heptene* [$\alpha\alpha\epsilon$-trimethyl-Δ^{δ}-hexenol], $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH$, a yellow oil boiling at 73—75° under 10·5 mm. pressure. It has a molecular refraction 44·72 and a sp. gr. at 20° 0·85496, n_D 1·45062 at 20°. Hydrogen bromide in acetic acid solution forms *$\beta\zeta$-dibromo-$\beta\zeta$-dimethylheptane*, crystallising from methyl alcohol in long needles and melting at 35°, converted by boiling with pyridine into *$\beta\zeta$-dimethyl-$\Delta^{\beta:\epsilon}$-heptadiene*, a colourless liquid of pleasant odour, which boils at 140—142° and does not form a crystallisable nitrosate or

tetrabromide. Ozone converts it, when moisture is excluded, into the *diozonide*, probably $O\!<\!\begin{matrix} O\cdot CMe_2 & CMe_2\cdot O \\ | \quad\; | & | \quad\;\; | \\ O\cdot CH\cdot CH_2\cdot CH & \!\!-\!\!-O \end{matrix}\!>\!O$, a colourless, viscous, highly explosive oil.

The dimethylheptenol described above is converted into *cyclo*geraniolene by boiling with phosphoric acid. Ozone forms an oily *ozonide*, $C_9H_{16}O_4$, having a sp. gr. at 20° 1·0983, n_D 1·46509 at 17°; the molecular refraction is 47·33. It boils at 80—100° under 10 mm. pressure, yielding a less viscous distillate. The constitution is unknown, four oxygen atoms having been added instead of three.

All these ozonides are decomposed violently by concentrated sulphuric acid, decolorise indigo solution, decompose potassium iodide, and form hydrogen peroxide with water. C. H. D.

Melting Points of Solid Chloroform, Toluene, and Ether. EBENEZER H. ARCHIBALD and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1904, 26, 305—306).—The melting points of pure chloroform, toluene, and ether were determined by means of the hydrogen thermometer, the results being corrected by Travers' method (Abstr., 1903, ii, 9). The following are the melting points obtained: chloroform, −63·2°; ether, −117·6°; toluene, −97° to −99°. E. G.

Electrolytic Preparation of Iodoform from Acetone. JOHN E. TEEPLE (*J. Amer. Chem. Soc.*, 1904, 26, 170—177).—A nearly theoretical yield of iodoform can be obtained by the electrolysis of a neutral solution of potassium iodide in presence of acetone, without the use of a diaphragm. The alkali produced must be neutralised as fast as it is formed; this may be effected by means of carbon dioxide, hydrochloric acid, hydriodic acid, or iodine. The temperature should not be allowed to rise above 25°, and the solution should be kept well stirred. A comparatively low anode current density and a high cathode density are required.

For a continuous process, it is probable that it would be best to neutralise the alkali by means of iodine. It was found by experiment that the yield is gradually decreased owing to the accumulation of potassium acetate, but that when the potassium acetate in the solution amounts to as much as 12 per cent., the yield of iodoform is not diminished by more than 15 per cent. E. G.

Derivatives of the Amyl Alcohols from Fusel Oil. IV. WILLY MARCKWALD (*Ber.*, 1904, 37, 1038—1052).—Details are given for preparing pure active amyl alcohol from fusel oil by first removing a large proportion of the inactive alcohol by taking advantage of its ready conversion by hydrogen chloride into amyl chloride, and subsequently working up the enriched product with 3-nitrophthalic acid (compare Abstr., 1901, i, 248).

A ready separation of the two alcohols cannot be effected by converting the mixture into the corresponding mixed urethanes and recrystallising the product, because the *d*-amylurethane dissolves in the *iso*amylurethane, forming mixed crystals; the converse, however,

is not true, as the *iso*amyl compound is only absorbed sparingly by the active urethane. Pure d-*amylurethane* melts at 61° and has $[\alpha]_D + 3{\cdot}32°$ in benzene solution; the pure *iso*amylurethane melts at 64·5°.

A systematic study has been made of the solubility of mixed crystals of the two barium amyl sulphates, which shows that a continuous increase of solubility accompanies an increase in the percentage of active salt; the curve connecting these quantities is parabolic.

d-Amyl alcohol, on oxidation, gives pure *d*-valeric acid having $a_D + 8{\cdot}75°$ for $l = 0{\cdot}5$. *d*-Amyl iodide cannot be obtained pure by the action of phosphorus iodide on the alcohol (compare Klages and Sautter, this vol., i, 302), as partial racemisation occurs; it is prepared therefore from hydrogen iodide and the alcohol. The following values show its rotatory dispersion: red, λ665·9, $[\alpha] + 4{\cdot}42°$; yellow, λ588·0, $[\alpha] + 5{\cdot}64°$; green, λ533·0, $[\alpha] + 6{\cdot}89°$; blue, λ488·5, $[\alpha] + 8{\cdot}20°$; dark blue, λ448·2, $[\alpha] + 9{\cdot}86°$; it has a sp. gr. 1·524 at 20°/4°. d-*Amyl bromide* boils at 118—120° and has a sp. gr. 1·221 at 20°/4° and $[\alpha]_D + 3{\cdot}68°$ at 20°. Pure *d*-methylethylpropylmethane [β-ethylpentane] (compare Just, Abstr., 1884, 169; Welt, Abstr., 1895, ii, 97) boils at 90—92° and has a sp. gr. 0·6865 at 20°/4° and $[\alpha]_D + 9{\cdot}5°$ at 20°.

Pure *iso*amylphthalimide, on cooling, solidifies and then melts at 12·5° (compare Neumann, Abstr., 1890, 890). d-*Amylphthalimide*, prepared from *d*-amyl bromide and potassium phthalimide, melts at 23°, boils at 303°, and, when liquid, has a sp. gr. 1·0930 at 25°/4°; it has $[\alpha]_D + 7{\cdot}53°$ at 25°. d-*Amylphthalamic acid* crystallises from benzene in white leaflets, melts at 123°, and, on hydrolysis with 10 per cent. sodium hydroxide solution, gives d-*amylamine*, which boils at 95·5—96°, has a sp. gr. 0·7505 at 25°/4°, and $[\alpha]_D - 5{\cdot}86°$ at 25°; the *platinichloride* of the base decomposes at 240°. The *hydrochloride* is hygroscopic, melts at 176°, and is inactive in solution, although racemisation has not occurred; this is shown by the pure active base being liberated by the addition of alkali.

Pure d-*amyl phenylcarbamate*, prepared from pure *d*-amyl alcohol and phenylcarbimide, forms white crystals, melts at 30°, and, in chloroform, has $[\alpha]_D + 6{\cdot}4°$ ($c = 5$) and $+ 6{\cdot}6°$ ($c = 15$); Goldschmidt and Freund's *d*-amyl phenylcarbamate (Abstr., 1894, ii, 405), although melting at the same temperature, had $[\alpha]_D = 4{\cdot}19°$, and contained only 65 per per cent. of the active ester. iso*Amyl phenylcarbamate*, prepared from *iso*amyl alcohol, melts at 55°. A melting point curve is given for mixtures of *d*- and *iso*-amyl phenylcarbamates. W. A. D.

Pentane-βδ-diol and βδ-Dibromopentane. A. Poray-Koschitz (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1112—1116).—*Pentane-βδ-diol*, $C_5H_{12}O_2$, prepared by reducing methyl β-hydroxypropyl ketone in aqueous solution by means of 3 per cent. sodium amalgam, is a colourless, viscous liquid, stable in the air and soluble in water and organic solvents; it boils at 197° under the ordinary pressure, and at 90—92° under 10 mm. pressure, and has the sp. gr. 0·96607 at 0°/0°. Its *diacetyl* derivative, $C_9H_{16}O_4$, is a colourless liquid, which boils at 84° under 8 mm. pressure and boils and decomposes at 200—210° under the ordinary pressure.

βδ-Dibromopentane, $C_5H_{10}Br_2$, prepared by the action of hydrobromic acid on pentane-2 : 4-diol in a sealed tube, boils at 63·5° under 9 mm. pressure, and has the sp. gr. 1·6789 at 0°/0°. T. H. P.

Monocarbon Compounds. Methylene Hydroxybromide. LOUIS HENRY (*Rec. trav. chim.*, 1904, 23, 16—25. Compare Favre, Abstr., 1895, i, 14, and Litterscheid, Abstr., 1901, i, 443).—In a previous communication (*Bull. Acad. roy. Belg.*, 1893, 615), the author has stated that the principal product of the action of hydrogen bromide on formaldehyde is methylene hydroxybromide (bromomethyl alcohol). He is now of opinion that this product is the hydrobromide of dimethyl ether, analogous in constitution to the hydrochloride described by Friedel (this Journ., 1875, 1245). T. A. H.

Preparation of the Lower Halogen-methyl Alkyl Ethers. FRANZ M. LITTERSCHEID (*Annalen*, 1903, 330, 108—112. Compare Abstr., 1901, i, 443).—A method of preparing the halogen-methyl alkyl ethers, $CH_2Cl·OR$, is described, which has advantages over that devised by Wedekind (D.R.-P., 1901, 135310). Molecular quantities of the alcohol and trioxymethylene (the former in slight excess) are mixed, and hydrogen chloride passed in until a liquid is obtained consisting of two layers; the lower is a saturated solution of hydrogen chloride, and the upper contains the halogenated ether. After addition of calcium chloride to remove alcohol, the latter is distilled, a yield of 85—95 per cent. being obtained. K. J. P. O.

Dichloromethyl Ether. FRANZ M. LITTERSCHEID (*Annalen*, 1903, 330, 112—117. Compare preceding abstract).—The *s*-dichloromethyl ether was prepared from the monochloromethyl ether (see preceding abstract) by passing a slow stream of dry chlorine for about 40 hours through the ether, which was kept at 12° in a place shaded from the light. The ether boiled at 103—106°.

When the dichloromethyl ether and pyridine are brought together in the presence of dry ether, a semi-crystalline mass separates, which can be converted into a *platinichloride*, $(C_5NH_5Cl·CH_2)_2O,PtCl_4$; the latter crystallises in large, reddish-yellow leaflets melting at 235°.

Strychnine forms a similar compound with dichloromethyl ether, the *platinichloride*, $(C_{21}H_{22}O_2N_2,CH_2Cl)_2O,PtCl_4$, of which forms a pale yellow powder decomposing at 240°. The *aurichloride* was obtained from the platinichloride, and crystallises in yellowish-brown needles, becoming coloured at 215° and melting at 220° K. J. P. O.

Chlorination of Chloromethyl Ethyl Ether. FRANZ M. LITTERSCHEID (*Annalen*, 1903, 330, 118—131. Compare preceding abstracts).—Chloromethyl ethyl ether, prepared by the action of hydrogen chloride on a mixture of trioxymethylene and ethyl alcohol, was treated with dry chlorine for about 100 hours in diffused daylight, and the product fractionated; four fractions were obtained, (i) b. p. 112—114°, (ii) b. p. 144—148°, (iii) b. p. 174—176°, and (iv) b. p. 205°. Fraction (i) contains the dichloride, $CH_2Cl·O·CHCl·CH_3$, since when heated with water it yields acetaldehyde and immediately gives up all its

chlorine to aqueous silver nitrate. Further, it reacts with pyridine in the proportion of 1 mol. of pyridine to 2 mols. of ether, forming a *compound* which yields a *platinichloride*,

$$(C_5NH_5Cl\cdot CH_2\cdot O\cdot CHMe\cdot C_5NH_5Cl),PtCl_4,$$

crystallising in microscopic plates melting and decomposing at 205°; the *aurichloride* melts at 178°. The dichloro-compound prepared by Henry (Abstr., 1895, i, 80) is the isomeride. It yields only one atom of chlorine when treated with silver nitrate, and combines only with 1 mol. of pyridine; the *platinichloride* of this additive product,

$$(C_5NH_5Cl\cdot CH_2\cdot O\cdot CH_2\cdot CH_2Cl)_2,PtCl_4,$$

crystallises in golden-yellow leaflets melting at 162°, the *aurichloride* forms lustrous, prismatic crystals melting at 84°.

Fraction (ii) is the compound $CH_2Cl\cdot O\cdot CHCl\cdot CH_2Cl$, since two atoms of chlorine can be eliminated by silver nitrate. With pyridine, it forms an additive product, from which the *platinichloride*,

$$C_5NH_5Cl\cdot CH_2\cdot O\cdot CH(CH_2Cl)\cdot C_5NH_5Cl,PtCl_4,$$

can be obtained in microscopic leaflets melting at 212°; the *aurichloride* forms microscopic crystals melting at 212°.

Fraction (iii) is the trichloride, $CH_2Cl\cdot O\cdot CHCl\cdot CHCl_2$; with pyridine, it yields an additive product, from which the *platinichloride*,

$$C_5NH_5Cl\cdot CH_2\cdot O\cdot CH(CHCl_2)\cdot C_5NH_5Cl,PtCl_4,$$

is obtained as a microcrystalline, yellowish-red powder melting at 224°.

Fraction (iv) was too small for accurate investigation; it consisted mainly of a tetrachloride. K. J. P. O.

Silver and Lead Salts of Alkyl Dihydrogen Phosphates. JACQUES CAVALIER (*Compt. rend.*, 1904, **138**, 762—763. Compare Abstr., 1900, i, 579; 1901, ii, 502, and Berthelot, Abstr., 1901, ii, 502, 503).—In respect of the solubility and stability of their lead and silver salts, ethyl and allyl dihydrogen phosphates closely resemble phosphoric acid, the normal salt being precipitated by lead or silver nitrate from a solution, neutral to methyl-orange, of the barium hydrogen alkyl phosphate, whilst the liquid becomes acid to the same indicator; the lead or silver hydrogen alkyl phosphates can only be formed in a strongly acid solution. The equation representing the formation of lead allyl phosphate from barium hydrogen allyl phosphate [1 mol. = 10*l*] and lead nitrate [1 mol. = 5*l*] is

$$2Ba[H(C_3H_5)PO_4]_2 + 2Pb(NO_3)_2 = Pb(C_3H_5\cdot PO_4)_2 + H_2(C_3H_5)PO_4 + 2Ba(NO_3)_2,$$

but the reaction is not complete, only about four-fifths of the theoretical quantity of the lead salt being formed. A yield of 52 per cent. of lead ethyl phosphate is obtained with solutions of similar concentration at the boiling point. The silver salts of ethyl and allyl dihydrogen phosphates are much more soluble than the corresponding lead salts, only 4 per cent. of the theoretical quantity of silver ethyl phosphate, Ag_2EtPO_4, being obtained from concentrated solutions of barium hydrogen ethyl phosphate [$Ba(EtHPO_4)_2 = 2l$] and silver nitrate [$2AgNO_3 = 2l$]. M. A. W.

Barium and Lead Uranyl Acetates. JOSEF ZEHENTER (*Monatsh.*, 1904, **25**, 197—219).—See this vol., ii, 344.

Marckwald's Asymmetric Synthesis of Active Valeric Acid. JULIUS B. COHEN and THOMAS S. PATTERSON (*Ber.*, 1904, 37, 1012—1014).—A criticism of Marckwald's views (compare this vol., i, 221).

W. A. D.

Some Derivatives of Racemic α-Campholytic and α-Campholenic Acids. GUSTAVE BLANC and L. DESFONTAINES (*Compt. rend.*, 1904, 138, 696—697).—A racemic campholytonitrile, boiling at 200—205°, can be obtained from the corresponding amide and phosphorus pentachloride; a dichloro-compound, $C_8H_{13}\cdot CCl_2\cdot NH_2$, which melts and partially sublimes at 175°, is also produced in this reaction. The nitrile so obtained is not pure, for on saponification it gives [as well as the original racemic campholytamide (melting at 103°)] an amide which melts at 171—172°. Campholytonitrile can be reduced with sodium and ethyl alcohol to an unsaturated base, $C_8H_{13}\cdot CH_2\cdot NH_2$, which boils at 184—185° and is insoluble in water, but dissolves readily in ordinary organic media. For the sake of comparison, *r*-α-aminocampholene, was prepared. It was obtained by the following steps: (1) dehydration of *r*-camphoroxime to *r*-α-campholenonitrile, $C_8H_{13}\cdot CH_2\cdot CN$, which boils at 228°; (2) saponification of this nitrile to *r*-α-campholenamide, which melts at 122° and gives (3), with bromine and sodium hydroxide, *r*-α-aminocampholene, $C_8H_{13}\cdot CH_2\cdot NH_2$, which boils at 184°. The oxamide of this base, $C_2O_2(NH\cdot C_9H_{15})_2$, melts at 134°, and the carbamide derivative, $NH_2\cdot CO\cdot NH\cdot C_9H_{15}$, at 115—116°. The corresponding derivatives furnished by the base obtained from *r*-α-campholytic nitrile are difficult to purify, the oxamide melts at 125°, and the carbamide at 112°. It is, however, probable that the two bases are identical, and that the slight differences are due to the latter compounds not being quite pure.

S. S.

Action of Dehydrating Agents on Hydroxypivalic Acid [β-Hydroxy-αα dimethylpropionic Acid]. EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 308—317).—When β-hydroxy-αα-dimethylpropionic acid, $OH\cdot CH_2\cdot CMe_2\cdot CO_2H$ (this vol., i, 219), is heated alone at 200° or is warmed with a 60 per cent. solution of sulphuric acid or with hydrochloric or hydrobromic acids (in this case a small quantity of bromopivalic acid is also formed), it is converted into a series of anhydrides of which the principal is a *product* ("hemipolylactide") for which the formula

$$OH\cdot CH_2\cdot CMe_2\cdot CO_2\cdot[CH_2\cdot CMe_2\cdot CO_2]_4\cdot CH_2\cdot CMe_2\cdot CO_2H,$$

is suggested. This substance forms white, microscopic needles, softens at 158°, and melts at 165°. It is nearly insoluble in most solvents, but dissolves in phenol and in boiling formic and acetic acids. When treated with solutions of potassium hydrogen carbonate or ammonia, it is converted into the respective salts, which are insoluble in water. When β-hydroxy-αα-dimethylpropionic acid is heated at 250—270°, it decomposes forming water, formaldehyde, *iso*butyric acid, *iso*butylene, and carbon monoxide and dioxide. The first two substances are regarded as produced by the direct decomposition of the acid, and the others, with the exception of the carbon monoxide, as due to the

gradual degradation of the hemipolylactide first formed. A scheme illustrating the course of this decomposition is given in the original.

T. A. H.

αα-Methylethylhydracrylic Acid. EDMOND E. BLAISE and L. MARCILLY (*Bull. Soc. chim.*, 1904, [iii], 31, 317—325).—Ethyl α-bromomethylethylacetate (Auwers and Fritzweiler, Abstr., 1898, i, 126), prepared by brominating the acid chloride and treating the resulting product with alcohol, was converted into *ethyl αα-methylethylhydracrylate*, $OH\cdot CH_2\cdot CMeEt\cdot CO_2Et$, by the general method already described (this vol., i, 218). This is a mobile liquid of pleasant odour; it boils at 108° under 25 mm. pressure. The *acetyl* derivative, obtained by acetylating the ester with acetyl chloride, boils at 113° under 20 mm. pressure.

αα-Methylethylhydracrylic acid crystallises from a mixture of ether and light petroleum, melts at 56°, is odourless, and dissolves in water and alcohol; the *potassium* salt crystallises from alcohol and melts at 262°, and the *phenylurethane*, $NHPh\cdot CO\cdot O\cdot CH_2\cdot CMeEt\cdot CO_2H$, separates from boiling water in slender needles, melts at 114—115°, and is soluble in alcohol. The acid, when oxidised with chromic acid, furnishes methylethylmalonic acid (m. p. 118°) and small quantities of α-methylbutaldehyde and carbon dioxide.

Quinine αα-methylethylhydracrylate separates from boiling water in slender, slightly yellow needles, melts at 177°, and dissolves in alcohol and benzene. This salt was fractionally crystallised from boiling water, but no separation into optical isomerides was thereby effected, the apparently least and most soluble fractions having $[\alpha]_D - 124°10'$ and $- 124°15'$ respectively. The *cinchonine* salt crystallises from benzene in slender needles, melts at 121—122°, and re-melts at 255°. When fractionally crystallised from benzene, the apparently least and most soluble fractions had $[\alpha]_D + 130°30'$ and $+ 130°36'$ respectively. The acid regenerated from the apparently least soluble fractions of the two salts was optically inactive. Attempts are now being made to deracemise the acid by the action of moulds.

T. A. H.

Action of Ethyl Succinate on Allyl Iodide in presence of Zinc. Synthesis and Properties of γ-Diallylbutyrolactone. ALEXANDER KASANSKY (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1179—1188).—The action of ethyl succinate on allyl iodide in presence of zinc results firstly in the formation of the compound

$$I\cdot ZnO\cdot C(C_3H_5)_2\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

which then undergoes change in two directions: (1) with 1 mol. of water it yields $I\cdot Zn\cdot OH + OH\cdot C(C_3H_5)_2\cdot CH_2\cdot CH_2\cdot CO_2Et$, the latter, with another mol. of water, then giving

$$EtOH + OH\cdot C(C_3H_5)_2\cdot CH_2\cdot CH_2\cdot CO_2H,$$

that is, γ-hydroxy-γγ-diallylbutyric acid, which was characterised by means of its *barium* and *calcium* salts. (2) It loses a molecule of water, yielding *γγ-diallylbutyrolactone*, $CH_2{<}{\begin{smallmatrix}CH_2\\CO\cdot O\end{smallmatrix}}{>}C(C_3H_5)_2$, which is a viscous liquid decomposed by water, but readily soluble in alcohol

or ether; it boils at 266—267°, and, under the action of an alkali or alkaline earth hydroxide, yields the corresponding salts of γ-hydroxy-γγ-diallylbutyric acid. With bromine, it forms an additive *compound*, $C_{10}H_{14}O_2Br_4$, which crystallises from alcohol in long, rectangular plates and melts and decomposes slightly at 125—127°. With hydrogen iodide, it gives *γ-iodo-γγ-diallylbutyric acid*, $CI(C_3H_5)_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which is obtained as a viscous, red liquid. Reduction of this iodo-acid by means of sodium amalgam in alcoholic solution yields *γγ-diallylbutyric acid*, $CH(C_3H_5)_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which boils at 264—267°; its *sodium* and *silver* salts were prepared and analysed; with bromide, it yields a tetrabromo-additive compound, which gradually loses hydrogen bromide, forming a lactonic derivative containing 3 atoms of bromine. Oxidation of γγ-diallylbutyrolactone by means of potassium permanganate gives a dibasic lactonic acid,

$$CH_2{<}{\begin{matrix}CH_2\text{—}\\CO\cdot O\end{matrix}}{>}C(CH_2 \cdot CO_2H)_2,$$

of which the *calcium* salt was prepared. T. H. P.

Behaviour at High Temperatures of Salts of the Dihydroxystearic Acid obtained by the Oxidation of Oleic Acid by Alkaline Potassium Permanganate Solution. NICOLAUS SAYTZEFF and ALEXANDER M. SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1193—1197).—On heating the calcium salt of θι-dihydroxystearic acid, $CH_3 \cdot [CH_2]_7 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H$, at 170° or the zinc salt at 185°, the corresponding salt of the keto-stearic acid,

$$CH_3 \cdot [CH_2]_7 \cdot CO \cdot [CH_2]_8 \cdot CO_2H,$$

prepared by Baruch (Abstr., 1894, i, 170), is obtained. The same acid, of which the *sodium*, *barium*, and *silver* salts were prepared and analysed, may be obtained by heating θι-dihydroxystearic acid with zinc chloride at 140°. T. H. P.

New Salts of Tervalent Cobalt and of Quadrivalent Uranium. N. A. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1247—1249).—On dissolving freshly-precipitated and washed cobalt hydroxide in a mixture of solutions of oxalic acid and ammonium oxalate, a green *double* salt is obtained having the composition

$$Co_2(C_2O_4)_3,2NH_4HC_2O_4,12H_2O;$$

it may be purified by dissolving in 30 per cent. alcohol, 50 per cent. methyl alcohol or water, and precipitating it from solution by means of strong alcohol or ether. It forms dark green plates or prisms, giving a bright green solution. Alkali hydroxides, barium hydroxide or carbonate, nitrous acid, potassium thiocyanate, potassium dichromate, or ferricyanide, or tannin are without action on solutions of the salt in the cold. Its reactions indicate the constitution

$$C_2O_4 \cdot [Co(C_2O_4 \cdot H) \cdot C_2O_4 \cdot NH_4]_2.$$

No similar salt of nickel could be prepared.

On dissolving uranium tetrafluoride in solutions of ammonium oxalate, a dark green liquid is obtained, which shows a violet fluorescence and deposits crystals of the double salt,

$$UF_4,2(NH_4)_2C_2O_4,4H_2O.$$

T. H. P

Diethyl*iso*succinic Acid. Auguste Lumière, Louis Lumière, and F. Perrin (*Bull. Soc. chim.*, 1904, [iii], 31, 350—351).—*Ethyl diethyl*iso*succinate*, $CHEt_2 \cdot CH(CO_2Et)_2$, prepared by the action of ethyl malonate on γ-iodopentane, $CHEt_2I$, in presence of sodium ethoxide dissolved in alcohol, is a liquid which boils at 242—245°. The corresponding *acid* crystallises in large, transparent tablets and melts at 52—53°; the *anilide* forms small, colourless needles melting at 219—220°. T. A. H.

Synthesis of αα-Dimethylglutaric Acid and of αα-Dimethyladipic Acid. Gustave Blanc (*Compt. rend.*, 1904, 138, 579—580).—αα-Dimethyl-γ-butyrolactone, $\begin{matrix} CMe_2-CO \\ | \\ CH_2 \cdot CH_2 \end{matrix}\!\!>\!O$, can be obtained by reducing ethyl αα-dimethylsuccinate with sodium and absolute alcohol. This lactone boils at 201—202° under atmospheric pressure, and, when heated in sealed tubes with dry potassium cyanide for 5 hours at 270°, yields a product, evidently potassium γ-cyano-αα-dimethylbutyrate, which may be hydrolysed to αα-dimethylglutaric acid melting at 85°. The synthetical product is identical with that obtained from *iso*lauronolic acid by oxidation.

Similarly, ethyl αα-dimethylglutarate gives αα-dimethyl-δ-valerolactone, $CH_2 < \begin{matrix} CMe_2 \cdot CO \\ CH_2 \cdot CH_2 \end{matrix} > O$, which boils at 105° under 13 mm. pressure and furnishes a barium salt crystallising with $1\frac{1}{2}H_2O$. This lactone, by treatment with potassium cyanide and subsequent hydrolysis, yields αα-dimethyladipic acid melting at 85—87°, and identical with the dimethyladipic acid already prepared from β-ionone or dihydro*iso*lauronic acid. From these reactions, it is evident that the reduction of αα-dimethylsuccinic and glutaric esters involves the carboxyl group attached to the primary carbon atom. S. S.

A Method of Preparing Aldehydes and Systematically Degrading Acids. Edmond E. Blaise (*Compt. rend.*, 1904, 138, 697—699).—When a lactide is distilled, decomposition ensues, and a considerable quantity of an aldehyde is formed,

$$CHR < \begin{matrix} CO \cdot O \\ O \cdot CO \end{matrix} > CHR = 2CO + 2R \cdot CHO;$$

at the same time, a small amount of an unsaturated acid is produced, $CH_2R \cdot CH < \begin{matrix} CO \cdot O \\ O \cdot CO \end{matrix} > CH \cdot CH_2R = 2R \cdot CH{:}CH \cdot CO_2H$. The aldehyde can be isolated from the distillate by fractionation; the yield varies from 50—60 per cent. of the theoretical. This reaction affords a means of degrading the fatty acids, the complete process involves four steps: (1) preparation of the α-monobromo-derivative, (2) replacement of bromine by hydroxyl, (3) heating the α-hydroxy-acid to obtain the lactide and distillation of the latter, (4) oxidation of the aldehyde to the corresponding acid. This process was carried out with hexoic, pelargonic, lauric, myristic, and palmitic acids. The following substances are described: *α-bromopelargonic acid* is a liquid; its *ethyl* ester boils at 138—140° under 24 mm. pressure. *α-Hydroxypelargonic acid* crystallises in plates, melts at 70°, and gives an *anilide* melting

at 69—70°, and an *ethyl* ester melting at 23—24°. *a-Acetoxypelargonic acid* is a liquid boiling and decomposing slightly at 171—174° under 10 mm. pressure. The aldehydes prepared are: n-*valeraldehyde* from hexoic acid, which gives an oxime melting at 52°; *n*-octaldehyde, from pelargonic acid, a liquid, which boils at 81° under 32 mm. pressure, and furnishes an oxime melting at 58—59°, a *phenylhydrazone*, which melts at 101°, and a diethylacetal, which boils at 221—223°. *Tridecanal*, from myristic acid, is a solid, which distils at 152° under 24 mm. pressure, and n-*pentadecanal*, from palmitic acid, is also a solid, which boils at 185° under 25 mm. pressure. S. S.

Action of Calcium Hydroxide on *iso*Butaldehyde. PETER HERRMANN (*Monatsh.*, 1904, 25, 188—196).—Lime water brings about the condensation of *iso*butaldehyde at the ordinary temperature to *iso*butaldol, $C_8H_{16}O_2$, together with traces of *iso*butyric acid. When milk of lime is employed, heat is developed and the condensation product contains, in addition to *iso*butaldol, octoglycol *iso*butyrate, $C_{12}H_{24}O_3$, which is identified by hydrolysis to octoglycol and *iso*butyric acid. The latter compounds are also found in small quantity in the condensation product, partial hydrolysis of the ester having taken place. The same products are obtained, with the addition of *iso*butyl alcohol, on heating *iso*butaldehyde with calcium hydroxide under pressure. C. H. D.

Synthetic *iso*Valeraldehyde and its Condensation Products. M. CIHLAR (*Monatsh.*, 1904, 25, 149—158).—The occurrence of the *iso*valerate of a glycol, $C_{10}H_{22}O_2$, in the condensation products of *iso*valeraldehyde with alkali, observed by Kohn (Abstr., 1896, i, 461; 1897, i, 396) and Rosinger (Abstr., 1901, i, 669), is contrary to the general rule given by Lieben (Abstr., 1896, i, 403). The aldehyde employed was prepared from fermentation amyl alcohol, and the formation of the ester is due to the presence of a certain quantity of γ-methylbutaldehyde.

Pure *iso*valeraldehyde may be synthetically prepared from *iso*butyl iodide by conversion into the cyanide, hydrolysis, conversion into the calcium salt, and distillation of a mixture of the calcium *iso*valerate and calcium formate. Or the *iso*valeric acid may be prepared by heating *iso*propylmalonic acid at 160—180°, and the calcium salt then distilled in the same way. The aldehyde boils at 92·5°. The *oxime* boils at 161·3° under 759 mm. pressure, and is converted by acetic anhydride into the *nitrile*, boiling at 129·2—130° under 743 mm. pressure.

When treated with alcoholic potassium hydroxide or dry potassium carbonate, *iso*valeraldehyde condenses, yielding *a-iso*propyl-*β-iso*butylacraldehyde, $CHMe_2{\cdot}CH_2{\cdot}CH{:}C(CHO){\cdot}CHMe_2$; no glycol ester is produced. C. H. D.

The Alkyl Allyl and Propenyl Ketones. EDMOND E. BLAISE (*Compt. rend.*, 1904, 138, 636—638. Compare this vol., i, 290).—The normal product of the condensation of allyl iodide and an alkyl nitrile is the alkyl ketone ($CH_2{:}CH{\cdot}CH_2{\cdot}COR$), the propenyl ketone

$$(CH_3{\cdot}CH_2{:}CH{\cdot}COR),$$

which is always present in the final product, being formed from the

former by an intramolecular change brought about by the action of sulphuric acid. The same change is effected readily by the halogen acids at the ordinary temperature, and even at $-80°$ in the case of hydrobromic acid, the final product being the corresponding alkyl β-bromopropyl ketone, $CH_3·CHBr·CH_2·COR$. A similar change occurs when the alkyl allyl ketone is heated with 10 per cent. solution of sulphuric acid, the product consisting of the alkyl propenyl ketone and the alkyl β-hydroxypropyl ketone, $CH_3·CH(OH)·CH_2·COR$. Owing to the readiness with which the alkyl allyl ketone is converted into the isomeric propenyl derivative, all attempts to prepare derivatives of the former by replacing the hydrogen atoms of the methylene group situated between the carbonyl radicle and ethylenic carbon atom have been unsuccessful; sodium ethoxide gives the corresponding β-ethoxypropyl ketone, $CH_3·CH(OEt)·CH_2·COR$, and formaldehyde in the presence of piperidine (compare Knoevenagel, Abstr., 1902, i, 226; 1903, i, 638) gives the isomeric propenyl ketone. M. A. W.

The Phenylcarbamates of Sugars. LÉON MAQUENNE and W. GOODWIN (*Compt. rend.*, 1904, 138, 633—636).—Tesmer (Abstr., 1885, 774; 1886, 49) showed that phenylcarbimide reacted with polyhydric alcohols belonging to the mannitol and sucrose series to give sparingly soluble phenylcarbamates. The authors have prepared similar compounds from some pentoses, hexoses, heptoses, and several polyoses by boiling the sugar with about $1\frac{1}{4}$ times the theoretical quantity of phenylcarbimide dissolved in two or three times its volume of dry piperidine. The compounds thus prepared are amorphous or microcrystalline, very sparingly soluble in the ordinary solvents, and have no sharp melting point, but decompose with evolution of a gas having the odour of phenylcarbimide. l-*Arabinose tetraphenylcarbamate*,

$$C_5H_6O_5(CO·NHPh)_4,$$

is a white, amorphous powder, insoluble in water, very slightly soluble in alcohol, and decomposes at about 250—255°. l-*Xylose tetraphenylcarbamate* is isomeric with the preceding compound and even less soluble in alcohol, and melts at about 265—270°. d-*Dextrose pentaphenylcarbamate*, $C_6H_7O_6(CO·NHPh)_5$, is an amorphous powder very slightly soluble in boiling alcohol and melts at about 255°. d-*Galactose pentaphenylcarbamate* is amorphous, slightly soluble in hot alcohol, and decomposes at 275°. *Lactose octophenylcarbamate*, $C_{12}H_{14}O_{11}(CO·NHPh)_8$, melts at about 275—280° and does not reduce Fehling's solution even after boiling with dilute sulphuric acid. *Trehalose octophenylcarbamate* is amorphous and melts at about 283°. *Melezitose undecaphenylcarbamate*, $C_{18}H_{21}O_{16}(CO·NHPh)_{11}$, is an amorphous powder melting at about 180° and slightly soluble in warm alcohol.

Contrary to Tesmer's experience, the authors find that the polyhydric alcohols give derivatives with phenylcarbimide in which each hydroxyl of the original compound is replaced by a carbamate residue, and the following compounds were prepared. *Mannitol hexaphenylcarbamate*, $C_6H_8O_6(CO·NHPh)_6$, melting at about 303°, is a powder consisting of very fine needles. From 100 parts of the sugar, 494 parts of the carbamate were obtained, theory requires 492.

Dulcitol hexaphenylcarbamate melts at 315° and closely resembles the preceding compound. *Perseitol heptaphenylcarbamate*,

$$C_7H_9O_7(CO{\cdot}NHPh)_7,$$

melts at 297° and is insoluble in boiling alcohol; 100 parts of the sugar yield 491 parts of the carbamate, the amount required by theory being 493.

Ethylcarbimide reacts with mannitol to yield a compound melting at 270° and containing the proportion of nitrogen required for a hexaethylcarbamate. M. A. W.

Condensation of Dextrose by Fusion with Ammonium Chloride. Hugo F. Klatt (*Annalen*, 1903, 329, 350—362).—After an historical *résumé* of the attempts to prepare synthetical dextrins (glucosins) from dextrose, an account is given of the dextrins obtained by heating dextrose with ammonium chloride.

An intimate mixture of anhydrous dextrose and 1 per cent. ammonium chloride was heated for varying times at 120—130°, and the product fractionated by dissolving in water and precipitating with alcohol; the earlier fractions were free from dextrose; the material was completely soluble in water, gave no phenylhydrazone or osazone with phenylhydrazine or *p*-bromophenylhydrazine, and no coloration with iodine, but readily reduced Fehling's solution (reducing power 10·1 about) and ammoniacal silver nitrate. The aqueous solution showed no mutarotation, and had $[\alpha]_D$ 94—100°. Analysis gave numbers closely agreeing with the formula $(C_6H_{10}O_5)_8,H_2O$, but mol. weight determinations by the freezing point method pointed rather to the formula $(C_6H_{10}O_5)_4,H_2O$. The most sparingly soluble fractions, which underwent no further change on fractionation, had $[\alpha]_D$ 105—106° and a reducing power of 10. The material did not ferment with yeast, nor was it attacked by diastase; by dilute acids, it was easily hydrolysed, forming dextrose; on oxidation with nitric acid, *d*-saccharic acid was alone produced. It is very doubtful if even the final fractions were exclusively composed of a single individual substance. The material appears to resemble closely, but does not seem to be identical with, the glucosins described by Grimaux (Abstr., 1886, 1003). K. J. P. O.

Glutamine. Eugène Sellier (*Chem. Centr.*, 1904, i, 789—790; from *Bull. Assoc. Chim. Sucr. Dist.*, 21, 754—760).—Glutamine has been isolated from the juice of the sugar beet; it is readily soluble in water at the ordinary temperature, less so in water at 0°, and only slightly so in alcohol. It is precipitated from its aqueous solution by alcohol in the form of very small, slender needles, which are occasionally grouped in star-shaped aggregates. After remaining for a few minutes with Nessler's reagent, glutamine gives the ammonia reaction.

Glutamine behaves as a very weak acid towards indicators, the acidity shown by phenolphthalein and rosolic acid increasing as the temperature rises, whilst with litmus and resazurine, temperature has no effect on the acidity. When distilled in a vacuum with lime at 36—40°, it loses a portion of its nitrogen in the form of ammonia, but under similar conditions magnesium oxide and barium carbonate do not cause liberation of ammonia. Glutamine has $[\alpha]_D$ +6·15° at 20°

in a 1 per cent. aqueous solution. The rotatory power is decreased by the addition of normal lead acetate, whilst basic lead acetate causes it to become lævorotatory, and acetic acid restores the rotatory power to its normal value.

Glutamine is completely precipitated by basic lead acetate only after remaining 8—10 hours. Since Schulze and Bosshard's glutamine was optically inactive (*Land. Ver. Stat.*, 29, 295), it would seem probable that optical isomerides may exist. E. W. W.

Decomposition of Lactose by Calcium Oxide. The Constitution of Parasaccharin. HEINRICH KILIANI and PETER LOEFFLER (*Ber.*, 1904, 37, 1196—1203).—Considerable quantities of parasaccharin, as well as *iso*saccharin and metasaccharin, are obtained from lactose when it is kept for some weeks in presence of calcium oxide. A modification of the former method of separation (compare Abstr., 1883, 565 and 962) is described. Parasaccharin, on oxidation with hydrogen peroxide and iron by Ruff and Fenton's method, yields *parasaccharopentose*, $C_5H_{10}O_4$, which crystallises in colourless prisms and plates, melts at 81·5—82°, and shows no optical activity. It forms a *phenylbenzylhydrazone* melting at 112—114°, and must have the following constitution: $OH\cdot CH_2\cdot CH_2\cdot CO\cdot CH(OH)\cdot CH_2\cdot OH$. The formula $OH\cdot CH_2\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot CH_2\cdot OH$ is therefore ascribed to parasaccharic acid.

The various saccharic acids form crystalline quinine salts, which may be used for their identification.

Quinine metasaccharate crystallises in little nodules from ether, melting at 134—135°, and soluble in 9·6 parts of cold 50 per cent. alcohol.

Quinine parasaccharate also melts at 134—135°, but is soluble in 0·93 part of 50 per cent. alcohol.

Quinine saccharate melts at 141—142°, whilst *quinine isosaccharate* melts at 191—192°, and is only sparingly soluble in cold water and cold 50 per cent. alcohol. E. F. A.

Compounds of Sucrose with some Metallic Salts. D. GAUTHIER (*Compt. rend.*, 1904, 138, 638—639. Compare this vol., i, 144).—Sucrose forms a crystalline compound with sodium iodide which has the composition $C_{12}H_{22}O_{11},NaI,2H_2O$ and not

$$2C_{12}H_{22}O_{11},3NaI,3H_2O,$$

as stated by Gill (this Journal, 1871, 272). Ammonium, potassium, sodium, and barium thiocyanates also form compounds with sucrose which crystallise in beautiful, prismatic crystals, and are represented by the formulæ $C_{12}H_{22}O_{11},NH_4CNS,1\cdot5H_2O$, $C_{12}H_{22}O_{11},KCNS,H_2O$, $C_{12}H_{22}O_{11},NaCNS,H_2O$, and $C_{12}H_{22}O_{11},Ba(CNS)_2,2H_2O$ respectively. M. A. W.

Hydrolysis of Maltose and of Dextrin by Dilute Acids and the Estimation of Starch. WILLIAM A. NOYES, GILBERT CRAWFORD, CHARLES H. JUMPER, EDGAR L. FLORY, and ROBERT B. ARNOLD (*J. Amer. Chem. Soc.*, 1904, 26, 266—280).—The hydrolysis of maltose and dextrin with hydrochloric acid proceeds at first approximately in accordance with the law of mass action, but afterwards becomes much

slower than would be expected. When maltose is heated with a 2·5 per cent. solution of hydrogen chloride, the maximum reducing power is attained in about an hour at 100° or in 20—30 minutes at 111°, and corresponds to a hydrolysis of 96—98 per cent. The reducing power of dextrose is not appreciably affected by this treatment. The hydrolysis of maltose is more complete in a solution of 2·4 per cent. strength than in one containing only 0·5 per cent. The rate of hydrolysis of dextrin with hydrochloric acid is only about one-half of that of maltose; after heating for an hour at 100°, 90 per cent. is hydrolysed, whilst after 2 hours the proportion hydrolysed is not quite 95 per cent.

When a solution of starch containing 0·5 per cent. is hydrolysed with extract of malt, the reducing power of the product after heating with hydrochloric acid indicates that it consists of 74—78 per cent. of maltose and 22—26 per cent. of dextrin. The hydrolysis of a solution of maize starch containing 0·5 per cent. with 2·5 per cent. hydrochloric acid amounts to 97 per cent. in an hour and 98 per cent. in 4 hours.

The following method is recommended for the estimation of starch. The starch is first converted into a mixture of maltose and dextrin by means of malt extract and, after filtration, 10 per cent. by volume of hydrochloric acid of sp. gr. 1·125 is added. The mixture is heated for an hour at 100°, and, when cold, a quantity of sodium hydroxide is added sufficient to neutralise 90 per cent. of the hydrochloric acid present; the solution is now made up to a definite volume, and the reducing power determined by means of Fehling's solution. One hundred parts of dextrose found in this manner correspond with 93 parts of starch in the original material. E. G.

Coagulation of Starch. Auguste Fernbach and Jules Wolff (*Ann. Inst. Pasteur*, 1904, 18, 165—180).—Malt extract contains a diastase (amylo-coagulase) which coagulates soluble starch. Coagulation was found to take place more readily at 8° than at 22°, whilst at higher temperatures, 26°, for example, no coagulation took place. The diastase is destroyed by heating for 5 minutes at 63°. Small amounts of soda were found to be favourable to coagulation, owing, perhaps, to its action on the amylase, which is more sensitive to soda than amylo-coagulase.

The coagulase was found to contain amylo-cellulose (Brown and Heron) in very variable amounts according to the conditions (temperature, time, &c.) under which it was produced (compare Maquenne, this vol., i, 17). N. H. J. M.

Amylocellulose formed by the Action of Diastase. Auguste Fernbach and Jules Wolff (*Compt. rend.*, 1904, 138, 819—821. Compare Abstr., 1903, i, 679; this vol., i, 17, 227, 228, 294).—The reversion of starch paste or its partial conversion into amylocellulose appears to be started initially by the action of diastase, and then to proceed spontaneously. Experiments made on the extent and rate of formation of amylocellulose in solutions of starch which had been heated to 120° showed that those solutions which had not been treated with malt extract, or those which had been treated with a small quantity of previously boiled malt extract, only contained traces of

amylocellulose even when left for 24 hours; whilst solutions which had been sown with a small quantity of unboiled malt extract contained large quantities of amylocellulose after being left for 24 hours, even if the solution, 15 minutes after mixing, had been heated to a temperature much higher than that required to destroy the diastase in malt extract. M. A. W.

[Stability of Schönbein's Gun-cotton.] A Correction. FRITZ FICHTER (*Ber.*, 1904, 37, 1074—1076).—Contrary to the statement contained in Will's lecture on explosives (*ibid.*, 291), the gun-cotton cartridges prepared by Schönbein in 1846 and kept in the Bernoullianum at Basle, are still completely active; one was fired after 25 years, and another, by Prof. Piccard, after 50 years, in connection with the Schönbein festival in 1899. T. M. L.

Dextrorotatory *sec.*-Butylamine. JOHANNES GADAMER (*Arch. Pharm.*, 1904, 242, 48—51).—An introduction to the following paper. C. F. B.

Alkylated *d*-Butyl-thiocarbamides and -carbamides. W. URBAN (*Arch. Pharm.*, 1904, 242, 51—85).—Alkylated *d*-butylthiocarbamides were prepared by heating *d*-butylthiocarbimide, CS:N·CHMeEt (essential oil of *Cochlearia officinalis*; Gadamer, Abstr., 1899, i, 534; 1901, i, 582), with amines of the type NH_2R', NHR_2', and NHR'' (including piperidine) in alcoholic solution. These thiocarbamides were converted into the corresponding carbamides, some (dissolved in slightly diluted alcohol) by digestion with moist yellow mercuric oxide at the ordinary temperature, others by warming a similar solution gently with silver nitrate, and nearly neutralising from time to time with barium hydroxide the nitric acid formed in the reaction.

Bromo- and iodo-propylene-*d*-butylthiocarbamides,

$$\begin{array}{l} \quad\;\; CH_2\cdot NH \\ CH_2Br\cdot CH\text{——}S \end{array}\!\!>C\cdot NH\cdot CHMeEt,$$

&c., were prepared by mixing bromine or iodine with *d*-butylallylthiocarbamide, CH_2:CH·CH_2·NH·CS·NH·CHMeEt, in ethereal solution, and decomposing with sodium hydroxide the hydrobromide, &c., that is formed. Chlorine, dissolved in carbon tetrachloride, seems to react in the same way as bromine and iodine, but a pure product could not be isolated.

Incidentally, r-sec.-*butyloxamic acid*, CO_2H·CO·NH·CHMeEt, melting at 88—89°, was prepared by heating with excess of oxalic acid at 180° the inactive *r-sec.*-butylamine obtained by reducing methylethylketoxime with sodium amalgam.

The melting points (m. p.) of the substances prepared are recorded in the accompanying table, and also the molecular rotations [M] (equal to [α] × mol. wt./100) in alcoholic and in chloroform solutions. The rotation was measured at 20° with sodium light, and in solutions of *N*/8 strength, except in one or two cases, where weaker solutions had to be used. The substances are tabulated in order of increasing

Substituted d-*Butyl-thiocarbamides, or* $\left.\begin{matrix}NHR'\\NR_2'\\ \text{or } NR''\end{matrix}\right\}$ $\cdot CS\cdot NH\cdot CHMeEt$, *and*

-carbamides, or $\left.\begin{matrix}NHR'\\NR_2'\\ \text{or } NR''\end{matrix}\right\}$ $\cdot CO\cdot NH\cdot CHMeEt$.

R′, or R_2', or R″.	M. p.	$[M]_D^{20°}$ in Alcohol.	$[M]_D^{20°}$ in Chloroform.	Mol. wt.	R.
[1] Hydrogen (*d*-butylcarbamide).	166°	+28·0°	[5] +32·0°	116·2	59·1
,, (*d*-butylthiocarbamide)	137	29·2	32·9	132·2	75·2
[2] Ethyl	92	—	—	—	—
Methyl (thio)	84	44·6	43·2	146·3	89·2
[2] Propyl	80	36·8	33·6	158·2	101·2
[2] *iso*Propyl	134	34·4	33·2	158·2	101·2
Ethyl (thio)	67	40·2	40·2	160·3	103·2
Dimethyl (thio)	54	108·0	72·6	160·3	103·2
[3] *n*-Butyl	47	32·4	32·4	172·2	115·2
[3] *r*-Butyl	132	42·4	30·8	172·2	115·2
d-Butyl	—	71·2	67·6	172·2	115·2
Allyl (thio)	31·5—32	36·2	35·0	172·3	115·2
Propyl (thio)	53	40·6	41·4	174·3	117·2
*iso*Propyl (thio)	112—112·5	36·8	34·6	174·3	117·2
Diethyl (thio)	60—60·5	66·0	51·8	188·3	131·2
n-Butyl (thio)	32	36·8	36·8	188·3	131·2
*iso*Butyl (thio)	51	36·8	43·6	188·3	131·2
r-Butyl (thio)	103	31·2	32·8	188·3	131·2
tert.-Butyl (thio)	132	28·8	35·6	188·3	131·2
d-Butyl (thio)	—	73·6	69·2	188·3	131·2
[2] Phenyl	150	46·4	[4] 53·2	192·3	135·2
Pentamethylene (thio)	114	128·4	78·8	200·3	143·2
*iso*Amyl (thio)	43—44	42·4	40·4	202·2	145·1
Phenyl (thio)	88	65·8	78·4	208·3	151·2
Benzyl	105	35·2	32·4	208·3	151·2
Hexyl (thio)	oil	32·0	31·2	216·3	159·2
[3] Benzyl (thio)	58	43·6	38·0	222·3	167·2
[3] Di*iso*butyl	84	55·2	46·8	228·3	171·2
Di*iso*butyl (thio)	33	68·8	49·6	244·3	187·2
Tetrahydroquinolyl (thio)	40	128·0	89·6	248·3	191·2
Tetrahydro*iso*quinolyl (thio)	117	99·2	66·4	248·3	191·2
Bromopropylene (thio)	92—93	55·6	52·4	251·2	194·1
α-Naphthyl (thio)	135	[4] 64·4	48·4	258·3	201·2
β-Naphthyl (thio)	120	67·6	77·6	258·3	201·2
Di*iso*amyl (thio)	oil	84·8	60·8	272·4	215·3
[3] Dibenzyl	69	52·4	48·4	296·2	239·1
Iodopropylene (thio)	114	59·2	54·0	298·1	241·0
Dibenzyl (thio)	56	56·0	30·2	312·3	255·2

[1] From butylamine sulphate and potassium cyanate.
[2] Prepared by means of mercuric oxide. [3] Prepared by means of silver nitrate.
[4] In $N/16$ solution. [5] In $N/32$ solution.

molecular weight; the weight of the fourth group, R, that is attached to the asymmetric carbon atom in addition to H, Me, and Et, is also tabulated.

Consideration of the table shows that the weight of this fourth group, R, has but little influence on the molecular rotation; also that the influence of the solvent is very marked. The introduction of a second alkyl group usually raises the molecular rotation, and more so in alcoholic than in chloroform solution. Among the butyl derivatives, the molecular rotation is greatest when the nitrogen atom is joined to CH_2, less when to CH, and least when to C. In almost all cases the carbamide has a smaller molecular rotation than the corresponding thiocarbamide. Comparison of allyl- with propyl-*d*-butylthiocarbamide shows that the presence of a $\gamma:\delta$ double linking lowers the rotation. The existence of a nitrogen atom in a closed ring increases the rotation, usually to an amount greater than that due to the presence of a closed ring merely attached to the nitrogen atom. No regularity can be detected in the influence of homologous groups. The rotation caused when two asymmetric carbon atoms are present cannot be represented as the sum of two rotations each caused by one of these atoms.

C. F. B.

Amino-alcohols of the Type $OH\cdot CMeR\cdot CH_2\cdot NMe_2$. ERNEST FOURNEAU (*Compt. rend.*, 1904, 138, 766—768).—By the action of a secondary or tertiary amine on Tiffeneau's chlorohydrins, $OH\cdot CMeR\cdot CH_2Cl$ (compare Abstr., 1902, i, 449), a yield of 80 per cent. of the corresponding amino-derivative is obtained. These amino-alcohols boil without decomposition under the ordinary pressure; the lower members of the series are very soluble in water, and they are all more soluble in cold than in hot water, and reduce acidified solutions of permanganate only on warming. Their salts crystallise with difficulty, and the double salts are either very soluble, as the mercurichlorides or platinichlorides, or are easily decomposed, as the aurichlorides; the corresponding benzoyl derivatives, however, crystallise well, and serve to characterise the parent base. The salts all possess the characteristic physiological property of inducing local anæsthesia. *Dimethylamino*-tert.-*butyl alcohol*, $OH\cdot CMe_2\cdot CH_2\cdot NMe_2$, boils at 60° under 48 mm. pressure, the *benzoyl* derivative crystallises from alcohol in large efflorescent cubes which melt at 202°.

Methylethyldimethylaminomethylcarbinol boils at 57° under 23 mm. pressure; the *hydrochloride* of the *benzoyl* derivative crystallises from alcohol in brilliant, slender needles melting at 175°; very soluble in water, methyl alcohol, or ethyl acetate; the *oxalate* melts at 145°.

Methylpropyldimethylaminomethylcarbinol boils at 78° under 35 mm. pressure; the corresponding *chlorohydrin* boils at 75° under 28 mm. The hydrochloride of the benzoyl derivative of the amino-alcohol, crystallises from a mixture of alcohol and ether in slender, hygroscopic needles which melt at 141°. The *chlorohydrin*, $OH\cdot CMe(C_5H_{11})\cdot CH_2Cl$, boils at 96° under 23 mm. pressure, and yields *methyl*iso*amyldimethylaminomethylcarbinol*, which boils at 98° under 24 mm. pressure, is sparingly soluble in water, and has a strong odour; the *hydrochloride* of the *benzoyl* derivative crystallises from a mixture of alcohol and

ether in brilliant, silky needles melting at 138° and insoluble in acetone. *Phenylmethyldimethylaminomethylcarbinol*, $OH\cdot CPhMe\cdot CH_2\cdot NMe_2$, boils at about 135—136° under 32 mm. pressure; the hydrochloride crystallises in spangles and melts at 159—160°; the hydrochloride of the benzoyl derivative crystallises from methyl alcohol in brilliant, flat crystals melting at 205—206°, and is sparingly soluble in alcohol or cold water.

The *chlorohydrin*, $OH\cdot CMe(CH_2Ph)\cdot CH_2Cl$, boils at 155° under 25 mm. *Benzylmethyldimethylaminomethylcarbinol* boils at 144° under 24 mm.; the *hydrochloride* of the *benzoyl* derivative crystallises from alcohol in slender needles or from methyl alcohol in large, transparent, hard prisms which melt at 195°. M. A. W.

Derivatives of Diacetonalkamines. MORITZ KOHN (*Monatsh.*, 1904, 25, 135—148. Compare Abstr., 1902, i, 349, and this vol., i, 18).—Sodium amalgam reduces an acidified solution of methyldiacetonamine, prepared from mesityl oxide and methylamine, to *methyldiacetonalkamine* [*methyl-β-methylamino*iso*butylcarbinol*],

$$NHMe\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH,$$

an oily liquid, with ammoniacal odour, boiling at 184·5—185·5° (uncorr.). The *platinichloride*, $(C_7H_{17}ON)_2,H_2PtCl_6$, is a yellow, crystalline precipitate. Dimethyldiacetonamine is reduced in similar manner to *dimethyldiacetonalkamine* [*methyl-β-dimethylamino*iso*butylcarbinol*], $NMe_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH$, a limpid liquid with ammoniacal odour boiling at 186—190°. The *platinichloride*, $(C_8H_{19}ON)_2,H_2PtCl_6$, is an orange-red, crystalline powder.

An attempt was made to prepare these compounds by methylation of methyl-β-amino*iso*butylcarbinol, but without success, an ammonium base being formed. The same base is obtained by methylation of methyl- or dimethyl-diacetonalkamines.

Diacetonalkamine [methyl-β-amino*iso*butylcarbinol],

$$NH_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH,$$

is best prepared by reduction of diacetonamine by sodium amalgam in hydrochloric acid solution (compare Kahan, Abstr., 1897, i, 494). Warming with methyl alcohol and methyl iodide converts it into a mixture of bases, consisting chiefly of methyldiacetonalkamine and a white solid. The latter compound is obtained in larger proportion when an excess of methyl iodide is employed. It is a methiodide containing admixed iodoform. When shaken with silver chloride, filtered, and precipitated by gold chloride, the *aurichloride*, $C_9H_{22}ONAuCl_4$, is obtained, crystallising from water in glistening, golden-yellow needles and melting at 157—159°. The *picrate*, $C_{15}H_{24}O_8N_4$, crystallises from alcohol in yellow leaflets and melts at 141—143°. The same product is obtained on methylating methyl- and dimethyl-diacetonalkamines; in the latter case, the *methiodide* was also isolated in the form of a white solid. The ammonium base formed must have the constitution $OH\cdot NMe_3\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH$, and is a homologue of homocholine, $OH\cdot NMe_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$ (Schmidt and Partheil, Abstr., 1892, 950). C. H. D.

Preparation of Ethyl Chloroaminocrotonate. ADRIAAN LINDNER and ROBERT BEHREND (*Annalen*, 1903, 329, 367).—Ethyl chloro-

aminocrotonate (Abstr., 1900, i, 210; 1902, i, 14) can be most readily prepared in yields of 71—76 per cent. by shaking an ethereal solution of ethyl aminocrotonate, cooled with ice, with the calculated quantity of potassium hypochlorite for a quarter of an hour; the ethereal solution is dried with sodium sulphate and evaporated, and the residue crystallised from petroleum. The hypochlorite solution is prepared by saturating a 10 per cent. solution of potassium hydroxide with chlorine, when a 6—8 per cent. solution of hypochlorite is obtained, which should not be acid nor contain a great excess of alkali hydroxide. K. J. P. O.

Condensation of Ethyl Aminocrotonate with Thiocarbimides. Robert Behrend and Paul Hesse (*Annalen*, 1903, 329, 341—350).—It has been previously shown (Abstr., 1901, i, 136) that with ethyl aminocrotonate, phenylthiocarbimide forms an additive product, ethyl iminoacetylphenylthiomalonamate, and, further, that these two substances condense together with elimination of alcohol, forming thionphenylmethyluracil. On treating the ester with silver carbonate in the presence of a small quantity of water, it is converted into ethyl iminoacetylmalonoanilate, which melts at 125—126° and is identical in all respects with the substance directly prepared from phenylcarbimide and ethyl aminocrotonate (*loc. cit.*). The ester is completely hydrolysed by boiling with hydrochloric acid, thus:

$$NH{:}CMe{\cdot}CH(CO_2Et){\cdot}CS{\cdot}NHPh + 5H_2O = H_2S + NH_3 + NH_2Ph + EtOH + CH_3{\cdot}CO_2H + CH_2(CO_2H)_2;$$

at the same time, a trace of phenylthiocarbamide appears to be formed.

When methylthiocarbimide is used instead of phenylthiocarbimide, corresponding reactions take place; *ethyl iminoacetylmethylthiomalonamate*, $NH{:}CMe{\cdot}CH(CO_2Et){\cdot}CS{\cdot}NHMe$, is prepared by heating a mixture of mol. proportions of methylthiocarbimide and ethyl aminocrotonate at 100°, and extracting the product with ether to remove unchanged material and with sodium hydroxide to remove methylthionuracil; the substance crystallises in prisms or needles of a pale yellow colour melting at 145—146°. On treatment with silver carbonate, it loses sulphur and is converted into *ethyl iminoacetylmethylmalonamate*, $NH{:}CMe{\cdot}CH(CO_2Et){\cdot}CO{\cdot}NHMe$, which forms colourless crystals melting at 124—126°. *Dimethylthionuracil*, $NMe<\begin{matrix}CO{\cdot}CH\\CS{\cdot}NH\end{matrix}>CMe$, is formed when the thiocarbimide and the ester are heated together at 150°, but only in a yield of 10 per cent.; it crystallises in white leaflets melting at 271—273°. The thionuracil is also produced when methylthiocarbimide and the ester are heated together at 100° with water, and when methylthiocarbamide is used instead of the carbimide. Ethyl acetoacetate and methylthiocarbamide do not yield the thionuracil.

On heating the dimethylthionuracil with concentrated hydrochloric acid under pressure at 160°, it is completely converted into 1:4-dimethyluracil (m. p. 261—262°; Behrend and Dietrich, 1900, i, 120). K. J. P. O.

Solubility of β-*l*-Asparagine and β-*l*-Aspartic Acid. HARRY W. BRESLER (*Zeit. physikal. Chem.*, 1904, 47, 611—617).—The solubility in each case increases as the temperature rises, as shown by determinations at various points between 0° and 100°. The variation of solubility with temperature is represented graphically and by formulæ.

J. C. P.

Alkyl Derivatives of Barbituric Acid. EMANUEL MERCK (D.R.-P. 146948, 146949, 147278, 147279, and 147280. Compare Abstr., 1903, i, 799).—The esters of dialkylmalonic acids condense with carbamide in presence of metallic ethoxides when the reacting compounds are heated together, alone or in alcoholic solution, forming CC-dialkylbarbituric acids. Alkali metals or their amides may be used in place of metallic ethoxides. The same derivatives are obtained from the acyl derivatives of carbamide, thus diethylbarbituric acid is obtained from ethyl diethylmalonate and acetylcarbamide or *propionylcarbamide*, the latter being prepared from propionyl chloride and carbamide, and melting at 209° (corr.).

Dimethylmalonic acid, carbamide, and phosphorus oxychloride form dimethylbarbituric acid, whilst the diethyl and higher derivatives form ureides of dialkylacetic acids (compare Abstr., 1903, i, 798). If, however, the dialkylmalonic acid is converted into the chloride by means of phosphorus chloride, the condensation with carbamide takes place readily: $CR_2(COCl)_2 + CO(NH_2)_2 = CR_2{<}{\begin{smallmatrix}CO\cdot NH\\CO\cdot NH\end{smallmatrix}}{>}CO + 2HCl$.

Esters of monoalkylmalonic acids also condense with carbamide in presence of alkali ethoxides. *Methylbarbituric acid*, $C_5H_6O_3N_2$, from diethyl methylmalonate, carbamide, and sodium ethoxide, crystallises from water in microscopic prisms or plates, and melts at 202—203° (corr.). The *sodium* salt, $C_{10}H_{11}O_6N_4Na$, crystallises in microscopic prisms containing water.

C. H. D.

[Preparation of Alkali Cyanides and Cyanamides.] DEUTSCHE GOLD- & SILBER-SCHEIDE-ANSTALT VORM. RÖSSLER (D R.-P. 148045 and 148046. Compare Abstr., 1902, i, 354).—Carbon reacts with sodamide or potassamide at 350—400°, forming the metallic derivative of cyanamide, $2NaNH_2 + C = Na_2N_2C + 2H_2$. Hydrocarbons, &c., may be employed in place of free carbon, or the alkali metal may first be fused, the requisite quantity of carbon then added, and ammonia passed into the mass, the temperature being maintained at first at 400°, and then, as the cyanamide is formed, gradually raised to 600°. On heating further to 800°, the reaction $Na_2N_2C + C = 2NaCN$ takes place. The sodium or potassium may also be employed in the form of an alloy with lead.

C. H. D.

Phosphorus-Nitrogen Bases of the Type $P(NHR)_3{:}NR$. PAUL LEMOULT (*Compt. rend.*, 1904, 138, 815—817. Compare Abstr., 1903, i, 672).—By the action of phosphorus pentachloride on *o*-toluidine or *as-m*-xylidine ($NH_2 : Me : Me = 1 : 2 : 4$), the homologues of trianilinophenylphosphimide in the form of their hydrochlorides are obtained,

together with the corresponding arylamide of orthophosphoric acid, $PO(NHR)_3$; the two are readily separated by the difference of their solubility in alcohol. The bases are much less stable than the corresponding aniline base, and have not been obtained in a free state, but the following salts are described: (1) from *o*-toluidine, the hydrochloride, $P(NH{\cdot}C_7H_7)_4Cl$, already described by Gilpin (compare Abstr., 1897, i, 463) can be obtained in beautiful needles 2—3 mm. long from concentrated hot alcoholic solution, which are active towards polarised light, melt and decompose at 254°, and are decomposed by alcoholic sodium hydroxide or sodium ethoxide, yielding *o*-toluidine; the *nitrate*, $P(NH{\cdot}C_7H_7)_4{\cdot}NO_3$, obtained by the action of alcoholic silver nitrate on the preceding salt, crystallises in beautiful, white, silky needles, melting at 250° and deflagrating at a higher temperature; the *platinichloride*, $[P(NH{\cdot}C_7H_7)_4Cl]_2,PtCl_4$, forms dull yellowish-red crystals, which are decomposed on boiling with alcohol, and blacken and decompose at 235—240°. (2) From *as-m*-xylidine, the *chloride*, $PCl(NH{\cdot}C_8H_9)_4$, crystallises from alcohol, melts and decomposes at 264°, and is decomposed by alcoholic alkali hydroxides yielding *as-m*-xylidine; the *nitrate*, $P(NH{\cdot}C_8H_9)_4{\cdot}NO_3$, obtained by double decomposition, melts and decomposes at 246—248°, and crystallises in beautiful, silky needles; the *platinichloride*, $[P(NH{\cdot}C_8H_9)_4Cl]_2,PtCl_4$, forms a pale red, sandy, crystalline precipitate which decomposes at 260°.

M. A. W.

Amphoteric Electrolytes, especially Cacodylic Acid. ARTHUR HANTZSCH (*Ber.*, 1904, 37, 1076—1084).—Zawidzki (Abstr., 1903, i, 801) has suggested that cacodylic acid acts as a pseudo-acid, because whilst its affinity constant is only $k = 4{\cdot}2 \times 10^{-7}$, as compared with $3{\cdot}0 \times 10^{-7}$ for carbonic acid, it still forms a neutral sodium salt, and he has further suggested as an alternative view that 'amphoteric electrolytes' behave in this way, and may yield neutral salts with bases, in spite of having exceedingly slight acid properties. That Zawidzki's conclusions are based on an incorrect interpretation of the experimental evidence is shown by the following considerations. There is nothing abnormal in the fact that cacodylic acid can be sharply titrated by using phenolphthalein as indicator, for it yields only a monobasic salt under these conditions, and carbonic acid can be equally sharply titrated; this was tested by preparing dilute aqueous solutions of carbonic acid by mixing an aqueous carbonate with the calculated quantity of acid, and titrating the carbonic acid by means of sodium hydroxide; the quantity of sodium hydroxide used exactly corresponded with the amount required to produce the salt $NaHCO_3$. Again, it can be calculated from the dissociation constant of cacodylic acid ($k = 4200 \times 10^{-10}$) that the sodium salt should be hydrolysed in $N/40$ solution to the extent of 0·11 per cent.; the actual values, 0·097, 0·093, 0·095, 0·096, 0·099, determined from experiments on the hydrolysis of ethyl acetate, are perfectly normal, and give no indication that cacodylic acid is anything but a simple weak monobasic acid.

That cacodylic acid has an exceedingly slight tendency to act as a dibasic acid is shown by the fact that on mixing sodium cacodylate

and sodium hydroxide in $N/9{\cdot}6$ solution at 25° the electrical conductivity is 25 units (10 per cent.) less than that calculated from a simple additive law, whilst in the case of sodium chloride the decrease is only 12·4 units, and in the case of sodium acetate 15·2 units; the effect is, however, very slight and entirely disappears in $N/48$ solution.

The view that cacodylic acid is an amphoteric electrolyte is based on the fact that it yields a chloride and a nitrate. It is pointed out, however, that these are not derived from cacodylic acid, but from the hydrate, and have the formulæ $AsMe_2(OH)_2Cl$ and $AsMe_2(OH)_2{\cdot}NO_3$, and not $AsMe_2O{\cdot}Cl$ and $AsMe_2O{\cdot}NO_3$, as should be the case if they were derived from an amphoteric cacodylic acid. Again, cacodylic acid, presumably in the form of the hydrate $AsMe_2(OH)_3$, from which the acid salts are derived, has a basic dissociation-constant, $4{\cdot}05 \times 10^{-13}$, and should be a stronger base than dimethylpyrone ($K = 2{\cdot}7 \times 10^{-13}$); this is shown to be the case by the fact that its hydrochloride is less dissociated and has a lower conductivity.

The author concludes that in aqueous solution there is an equilibrium between cacodylic acid, which is ionised as an acid and yields metallic salts, $AsMe_2O{\cdot}\overset{-}{O}/\overset{+}{H} \rightarrow AsMe_2O{\cdot}\overset{-}{O}/\overset{+}{Na}$, and its hydrate, 'cacodyl base' or 'cacodyl alcohol,' which is ionised as a base and yields salts with acids, $AsMe_2(O\overset{+}{H})_2/\overset{-}{O}H \rightarrow AsMe_2(O\overset{+}{H})_2/\overset{-}{Cl}$. T. M. L.

Catalytic Preparation of Organic Aluminium Compounds. J. A. Fürstenhoff (*Chem. Centr.*, 1904, i, 785—786; from *Bull. Assoc. Belge Chim.*, 17, 414—426).—Aluminium does not act on cold ethylene dibromide, but at a temperature near the boiling point of the latter a compound is formed which has probably the composition

$$AlBr_3,Al(C_2H_4Br)_3.$$

When a few drops of this compound are added to a mixture of aluminium and ethylene dibromide, the action takes place at the ordinary temperature, and in a similar manner aluminium acts on ethyl bromide in presence of this compound. The aluminium bromoalkyl compounds fume in the air, ultimately taking fire and forming dense acid fumes. Gustavson has prepared similar substances, but at higher temperatures, and they are probably, therefore, decomposition products of aluminium bromoalkyl compounds. E. W. W.

Quadrivalent Oxygen. Julius von Braun (*Chem. Centr.*, 1904, i, 867—868; from *Nachr. k. Ges. Wiss. Göttingen*, 1903, 331—335). —Acid amides react energetically with halogen alkyls in the presence of zinc or magnesium or with magnesium halogen alkyloxides; in some cases, the heat developed is sufficient to char the whole mass. The violence of the action may be moderated by dilution with benzene or ether. The products obtained resemble those prepared by the action of zinc and halogen alkyls on ketones or aldehydes; they are in most cases amorphous, gummy substances, and are readily soluble in benzene, but only slightly so in ether or light petroleum. These compounds contain carbon, nitrogen, metal, and halogen, and are

probably formed by the action of molecular proportions of amide and metal. They may be hydrolysed, but not so readily as magnesium halogen alkyloxides, and then form the original acid amide and the hydrocarbon corresponding with the halogen alkyl used in their preparation. By the action of dilute sulphuric acid on the products prepared by the action of zinc and methyl iodide or propyl iodide respectively on diethylacetamide or dipropylacetamide, a 95 per cent. yield of the original amide and methane or propane is obtained. This reaction indicates a constitution of the type $\begin{matrix}R\\RN_2\end{matrix}{>}C{:}O{<}\begin{matrix}MeCl\\R\end{matrix}$. E. W. W.

Structure of Heptanaphthylenes and some of their Compounds. WLADIMIR B. MARKOWNIKOFF (*J. Russ. Phys. Chem.*, 1903, 35, 1049—1072).—The oxidation of the heptanaphthylene, prepared by the action of alcoholic potassium hydroxide on heptanaphthylene hydrobromide, by means of concentrated nitric acid yields mainly β-methyladipic acid, together with a small quantity of a-methyladipic acid. The heptanaphthylene therefore consists of a mixture of two constituents, the principal one having the double linking in the 3 : 4-position, and the other in the 2 : 3-position, the methyl group being in the 1-position.

The heptanaphthylene obtained from the xanthic ester, when oxidised with permanganate, yields succinic and oxalic acids, and must hence have the 3 : 4-structure. Its formation takes place according to the following equation: $\begin{matrix}CH_2{\cdot}CH_2{-\!\!-}CH{\cdot}O{\cdot}CS_2Me\\ CH_2{\cdot}CHMe{\cdot}CH_2\end{matrix} = \begin{matrix}CH_2{\cdot}CH{=\!\!=}CH\\ CH_2{\cdot}CHMe{\cdot}CH_2\end{matrix} + COS + CH_3{\cdot}SH.$

The action of aqueous sulphuric acid (1 vol. acid to 1 of water) on 3 : 4-methylnaphthylene converts it partly into the 2 : 3- and 1 : 2-isomerides and partly into ordinary 3-methylhexanol ($Me : OH = 1 : 3$), the inactive stereoisomeride of the latter and 2-methylhexanol.

When treated with sulphuric acid diluted with half its volume of water, 3 : 4-heptanaphthylene undergoes polymerisation, yielding: (1) *diheptanaphthylene*, $\begin{matrix}CH_2{\cdot}CH_2{-\!\!-}CH{-\!\!-}C{=\!\!=\!\!=}CH{\cdot}CH_2\\ CH_2{\cdot}CHMe{\cdot}CH_2\quad CH_2{:}CHMe{\cdot}CH_2\end{matrix}$, which is a viscous, colourless liquid having the sp. gr. 0·9128 at 0°/0° and 0·9119 at 20°/0°; and a_D +0·28° in a 5 cm. tube. It instantly decolorises bromine, but not permanganate, whether in the pure state or in solution; with the former, it gives a dibromide, $C_{14}H_{24}Br_2$, and a dibromide of its monobromo-derivative, $C_{14}H_{23}Br_3$.

From these results and others previously obtained, the author draws the following conclusion. In the most simple form of six-membered cyclic hydrocarbon containing one substituted radicle, the influence of the latter is such that both in the splitting-off of hydrogen, together with a halogen or other group, and in the combination with a molecule containing mobile hydrogen, the latter splits off from, or combines preferably with, the carbon atom furthest removed from the side-chain, whilst the electro-negative element combines with the carbon nearest the side-chain. T. H. P.

Cyclic Compounds. Heptanaphthylenes or Methyl*cyclo*hexenes. Wladimir B. Markownikoff (*J. Russ Phys. Chem. Soc.*, 1904, 36, 39—62).—After referring to the work of other authors on the heptanaphthylenes, the author gives the properties of 1-methyl-$\Delta^{3.4}$-*cyclo*hexene (see Markownikoff and Stadnikoff, Abstr., 1903, i, 803) and some of its derivatives.

The *dibromide*, $C_7H_{12}Br_2$, is a colourless oil boiling at 130° under 40 mm. pressure; it has a strong camphor-like odour, and it gradually decomposes at the ordinary temperature; it has a sp. gr. 1·650 at 15°/15°, and 1·648 at 20°/15°, and $[\alpha]_D$ 9·01° at 20°. The *nitroso-chloride*, $C_7H_{12}ONCl$, is a stable, heavy liquid with a pungent odour and a bright bluish-green colour; with alcoholic potassium hydroxide, it gives the original 1-methyl-$\Delta^{3.4}$-*cyclo*hexene. The iodide of the latter yields, with silver acetate, an inactive stereoisomeric *methyl*cyclo*hexene* which boils at 103·5° under 767 mm. pressure and has the sp. gr. 0·8172 at 0°/0°, 0·7999 at 20°/0°, and 0·80305 at 20°/15°.

1-Methyl-$\Delta^{2.3}$-*cyclo*hexene was not obtained quite free from the $\Delta^{3.4}$-isomeride; it has a lower specific rotation than the latter, and boils at about 105° under 760 mm. pressure.

1-*Methyl*-$\Delta^{1.2}$-cyclo*hexene*, $CMe{<}\begin{matrix}CH_2\cdot CH_2\\ CH{-}CH_2\end{matrix}{>}CH_2$, is an optically inactive liquid with an odour resembling that of turpentine; it boils at 106—108° (mainly at 107·5°) under 750 mm. pressure and at 108—110° (mainly at 109°) under 768 mm. pressure; it has the sp. gr. 0·81658 at 0°/0°, 0·80054 at 20°/0°, and 0·80167 at 20°/20°, its coefficient of expansion from 0° to 20° being 0·00082; it oxidises in the air even more rapidly than the $\Delta^{3.4}$-isomeride. If a drop of the hydrocarbon is mixed with 10 c.c. of alcohol and sulphuric acid then carefully added, the surface of separation of the two layers becomes coloured bright yellow, which quickly changes to orange, while the upper alcoholic liquid turns blue; on shaking, the whole of the liquid assumes a bright green colour with a blue tint.

The work of Morris (Trans., 1882, 167), Rénard (Abstr., 1887, 565), and Maquenne (Abstr., 1889, 32 and 361; 1892, 1065) is discussed.

T. H. P.

Friedel and Crafts' Reaction. IV. Jacob Boeseken (*Rec. trav. chim.*, 1904, 23, 98—109. Compare Abstr., 1900, i, 349; 1901, i, 474; 1903, i, 617 and 626).—The resinous substance, C_7H_6, produced by the interaction of aluminium chloride with benzyl chloride may be composed of a ring of *n* groups of the type $C_6H_4\cdot CH_2$ or $C_6H_5\cdot CH$; the latter is the more probable, since a similar resinous product is obtained from either *p*-chloro- or *p*-bromo-benzyl chloride, whereas if the union were effected through the benzene ring, as a structure of the first type would imply, the introduction of a haloid atom in the *para*-position should inhibit, or at least diminish, the formation of resinous products. The production of the latter appears to depend on the simultaneous occurrence of hydrogen and chlorine atoms in the side-chain, since they are not formed when aluminium chloride reacts with diphenylmethane, diphenyldichloromethane, or triphenylmethane. In

this connection, the instability of *iso*butyl chloride and of diphenylchloromethane towards aluminium chloride is of interest (Abstr., 1903, i, 617).

p-Nitrobenzyl chloride behaves differently (compare Perrier, Abstr., 1895, i, 510), forming with aluminium chloride an additive *product* (yellow spangles, stable at 100°) which reacts with benzene and its homologues at 50°, furnishing the corresponding *p*-nitrodiphenylmethanes. This additive product appears to be partially dissociated when dissolved in benzene, and it is perhaps the aluminium chloride so liberated which brings about the catalytic action. The author now regards the formation of such additive products as of secondary importance in the aluminium chloride condensation; they merely serve to increase the yield by preventing the destructive action of the condensing agent on the product formed. He also does not accept Kronberg's view as to the constitution of the additive compound of benzoyl chloride (Abstr., 1900, i, 502) with aluminium chloride, but prefers the formula $C_6H_5\cdot CCl\colon O<^{Cl}_{AlCl_2}$.

In the condensation of acyl chlorides with aromatic hydrocarbons or their derivatives, para-substituted ketones are almost invariably produced. This appears to be due to the directive influence of the aluminium chloride, which, it is suggested, is unable to form additive compounds of the type $C_6H_5\cdot CO(AlCl_3)\cdot C_6H_4X$ with the substituent X in the ortho-position to the carbonyl. In the compounds of aluminium chloride with *p*-nitrodiphenylmethane and its derivatives, combination occurs at a different part of the molecule, and consequently this directive influence is no longer exerted. When *p*-nitrobenzyl chloride is condensed with benzene, *p*-nitrodiphenylmethane alone is formed, but with toluene an oily mixture of isomerides is produced, and with chlorobenzene a mixture of *p*-chloro-*p*-nitrodiphenylmethane (melting at 104°) and o-*chloro*-p-*nitrodiphenylmethane* (?), large crystals, melting at 67°. The corresponding bromo-derivatives are similarly obtained from bromobenzene; o-*bromo*-p-*nitrodiphenylmethane* (?) crystallises in long needles and melts at 73°. T. A. H.

Aromatic Propylene Compounds. IV. *iso*Eugenol Ethyl Ether. CARL HELL and HERMANN BAUER (*Ber.*, 1904, 37, 1128—1132. Compare Abstr., 1896, i, 20; 1903, i, 242, 479; this vol., i, 241; also Zincke, this vol., i, 41).—Aromatic propylene dibromides are divided into three groups. (1) Stable dibromides such as the dibromides of phenylpropylene and of *o*-anethole. These may in certain cases be distilled without decomposition, and are not acted on by water or alcohol. (2) Dibromides so unstable that they cannot be isolated, but immediately lose hydrogen bromide and yield bromopropylene compounds, for example, the dibromides of diphenylpropylene, phenylmethylpropylene, and phenylanisylpropylene. (3) Dibromides which are moderately stable, and which slowly react with water or alcohol, for example, the dibromides of *iso*eugenol ethers and of anethole.

*iso*Eugenol ethyl ether dibromide when treated with aqueous acetone at 40° loses hydrogen bromide (2 mols.), and with methyl

alcohol at the ordinary temperature yields

$OMe \cdot C_6H_3(OEt) \cdot CH(OMe) \cdot CHMeBr$,

melting at 69—70°.

Bromoethyleugenole, on treatment with alcoholic potash, is converted into the corresponding *iso*eugenole derivative, which readily forms an oily *dibromide*. With water, this dibromide yields *2-bromo-3-methoxy-4-ethoxy-1-β-bromo-α-hydroxypropylbenzene*,

$OEt \cdot C_6H_2Br(OEt) \cdot CH(OH) \cdot CHBrMe$,

melting at 106—107°. The corresponding *methyl* ether melts at 63—64°. *Dibromoethyl* iso*eugenole*, $OMe \cdot C_6HBr_2(OEt) \cdot CH{:}CHMe$, obtained from dibromoethyleugenole (Abstr., 1895, i, 656), crystallises in long, pale rose-coloured needles melting at 79·5°, and yields a *dibromide*, which melts at 70—71°. With warm water, the dibromide is slowly decomposed, yielding *2 : 5-dibromo-3-methoxy-4-ethoxy-1-α-hydroxy-β-bromopropyl benzene*, $OMe \cdot C_6HBr_2(OEt) \cdot CH(OH) \cdot CHBrMe$, melting at 102—103°. The corresponding *methyl ether* melts at 63—64°.

J. J. S.

Ozonides of Simple Unsaturated Hydrocarbons. CARL D. HARRIES and ALFRED S. DE OSA (*Ber.*, 1904, 37, 842—845).—The product of the distillation of γ-amino-α-phenylbutane phosphate (Abstr., 1903, i, 815) is a mixture of α-phenyl-Δ^{α}-butylene and α-phenyl-Δ^{β}-butylene. Klages' method (Abstr., 1902, i, 669) yields pure α-phenyl-Δ^{β}-butylene, which does not form a nitrosite.

α-Phenyl-Δ^{β}-butylene ozonide, $C_{10}H_{12}O_3$, prepared by the action of ozone at a low temperature in complete absence of water, is a viscid, colourless, pungent-smelling syrup, exploding when heated on platinum foil, insoluble in water, but dissolving, probably with decomposition, in ether and alcohol. When distilled under 12 mm. pressure, a mobile liquid passes over, which has, however, the same composition, and the molecular weight of which corresponds with the formula $C_{10}H_{12}O_3$.

α-Phenyl-γ-methyl-Δ^{β}-butylene ozonide, $CH_2Ph \cdot CH{<}{\scriptstyle\begin{matrix}CMe_2\\|\\O_3\end{matrix}}$, is also a colourless, viscous oil.

In the action of ozone on phenylbutylene in presence of water, phenylacetaldehyde is produced, and not hydrocinnamaldehyde, as formerly stated. C. H. D.

***iso*Amenyl-benzene and -toluene.** FRANZ KUNCKELL and KARL ARTHUR STAHEL (*Ber.*, 1904, 37, 1087—1090).—A method is described by which *iso*amenylbenzene can be prepared with greater readiness than when using the method described by Schramm (Dafert, Abstr., 1883, 1094).

*Phenyl α-bromo*iso*butyl ketone*, $COPh \cdot CHBr \cdot CHMe_2$, prepared by the action of aluminium chloride on a solution of α-bromo*iso*valeryl bromide and benzene in carbon disulphide, crystallises from alcohol in colourless flakes and melts at 47°.

*α-Chloro-β-bromo*iso*amenylbenzene*, $CPhCl{:}CBr \cdot CHMe_2$, prepared by the action of phosphorus pentachloride on the preceding compound, is a colourless oil, which boils at 125—129° under 10 mm. pressure, decomposes when distilled under atmospheric pressure, and has a sp. gr.

1·28 at 15°; it is reduced by metallic sodium in ethereal solution to *iso*amenylbenzene.

p-*Tolyl a-bromo*iso*butyl ketone*, $CH_3·C_6H_4·CO·CHBr·CHMe_2$, crystallises from alcohol in flakes and melts at 57°.

*a-Chloro-β-bromo*iso*amenyltoluene*, $CH_3·C_6H_4·CCl:CBr·CHMe_2$, is an oil which boils at 130—140° under 16 mm. pressure, becomes green when kept, and has a sp. gr. 1·303 at 18°.

p-iso*Amenyltoluene*, $CH_3·C_6H_4·CH:CH·CHMe_2$, is a colourless, aromatic oil, which boils at 106—107° under 10—11 mm. pressure, and has a sp. gr. 0·885 at 18°/4°, and n_D 1·5316 at 20°.

*aβ-Dibromo*iso*amyltoluene*, $CH_3·C_6H_4·CHBr·CHBr·CHMe_2$, crystallises from alcohol in colourless flakes and melts at 85°. The corresponding *di-iodide* crystallises from alcohol in pearly flakes and melts at 106—107°.

The boiling point of 1:2-dimethyl-4-allylbenzene is 110—112° under 16 mm. pressure, and not 165—168° as previously stated (Abstr., 1903, i, 617). T. M. L.

Aromatic Nitro-compounds. XVII. Comparative Study of the Three Dinitrobenzenes. IV. Action of Potassium Cyanide. CORNELIS A. LOBRY DE BRUYN and J. W. VAN GEUNS (*Rec. trav. chim.*, 1904, **23**, 26—38. Compare Abstr., 1885, 656, 657; 1891, 429; 1894, 573; 1899, i, 744, 745; and 1901, i, 460).—When a mixture of dry potassium cyanide and dinitrobenzene is heated, gas begins to be evolved at 160°, and if the temperature is very slowly raised to 210° the principal product is 2:2′-dinitrodiphenyl ether (Haeussermann and Bauer, Abstr., 1896, i, 676).

When an aqueous solution of potassium cyanide is employed, small quantities of *o*-nitrophenol and potassium cyanate and nitrite are produced, but most of the dinitrobenzene is recovered unchanged.

m-Dinitrobenzene begins to react with dry potassium cyanide at 160°, but as the temperature is raised to 235° complete decomposition ensues. With an aqueous solution of potassium cyanide, brown, humus-like decomposition products are formed.

p-Dinitrobenzene, when heated at 200—208° with dry potassium cyanide, gives off a gas having the percentage composition: nitric oxide 35, carbon dioxide 28, nitrogen 41. The principal product of the reaction is the di-*p*-nitrophenyl ether, described by Haeussermann and Teichmann (Abstr., 1896, i, 533). With an aqueous solution of potassium cyanide, ammonium carbonate and hydrocyanic acid are formed in addition to *p*-nitrophenol and 4:4′-dinitroazobenzene and 4:4′-dinitroazoxybenzene (Abstr., 1900, i, 194), the last mentioned being the principal product.

The interactions of the three dinitrobenzenes with potassium cyanide dissolved in alcohol have already been described (Abstr., 1885, 656 and 657). The authors are unable to confirm the observation of Hodgkinson and Hope (*Chemical News*, 1899, 20), that by the action of *m*-dinitrobenzene on dry potassium cyanide in dry alcohol, nitrobenzonitrile and not ethoxynitrobenzonitrile is produced; they find, however, that the presence of some water in the alcohol is essential to the formation of the latter.

Propoxynitrobenzonitrile, $NO_2 \cdot C_6H_3(OPr^{\alpha}) \cdot CN$ [$CN : NO_2 : OPr_{\alpha}$ = 1 : 2 : 6], produced in small amount by the action of potassium cyanide on *m*-dinitrobenzene dissolved in propyl alcohol, crystallises in slightly yellow, lustrous spangles, melts at 105°, and resembles its lower homologues in properties.

When *p*-dinitrobenzene is treated with potassium cyanide dissolved in methyl alcohol, *p*-nitroanisole is produced; with ethyl alcohol as a solvent, *p*-nitrophenetole is obtained. In both cases some 4 : 4′-dinitroazobenzene is also formed. T. A. H.

Aromatic Nitro-compounds. XVIII. Comparative Study of the Three Dinitrobenzenes. V. Summary of Results. Cornelis A. Lobry de Bruyn (*Rec. trav. chim.*, 1904, **23**, 39—46).—A summary of the results of work already published by the author and collaborators (Abstr., 1885, 656, 657; 1891, 428; 1892, 305; 1894, 573; 1895, i, 654; 1899, i, 744, 745; 1900, i, 460, 461, 462, and preceding abstract).

The results show that the three dinitrobenzenes behave similarly towards hydrochloric acid and the halogens, the nitro-groups being wholly replaced in the ortho-compound and partially in the meta- and para-isomerides (only one nitro-group is replaced in the latter). In all other reactions, well-marked differences in behaviour are shown between the ortho- and meta-isomerides, and frequently also between the meta- and para-compounds. Examples of these differences are quoted from the previous papers. T. A. H.

Aromatic Nitro-compounds. XIX. Action of Potassium Cyanide. Cornelis A. Lobry de Bruyn (*Rec. trav. chim.*, 1904, **23**, 47—61).—The changes induced by the action of potassium cyanide on aromatic nitro-compounds may be conveniently classified into three groups.

(1) *The reduction of the nitro-compounds, especially to azo-, azoxy-, and nitroso-derivatives or to amino- or hydroxy-compounds with the formation of potassium cyanate.*—Examples of such reactions are (*a*) the conversion of *o*-nitrobenzaldehyde into *o*-azoxybenzoic acid (Homolka, Abstr., 1884, 1342), in which case it is suggested that the aldehyde is first changed into *o*-nitrosobenzoic acid under the influence of light, and this is then reduced by the cyanide; (*b*) the action of potassium cyanide on dinitrophenols (Nietzki and Petri, Abstr., 1900, i, 485; Borsche, *ibid.*, 645; and with Locatelli, 1902, i, 226), and (*c*) the action of potassium cyanide on dinitrobenzenes (Lobry de Bruyn and Van Geuns, preceding page).

(2) *The replacement of the nitro-group by alkoxy-groups when the cyanide is used in alcoholic solution.*—Examples of this reaction are the formation of dinitroanisole from 1 : 2 : 4-trinitrobenzene and of alkoxynitrobenzonitriles from *m*-dinitrobenzene by the action of potassium cyanide dissolved in alcohols (Abstr., 1885, 657).

(3) *The introduction of cyano-groups either* (a) *by replacement of a nitro-group or* (b) *by indirect substitution of a hydrogen atom adjacent to a nitro-group.*—An example of the first type has recently been observed by Van Geuns in the author's laboratory, namely, the con-

version of alkoxydinitrobenzonitriles into dicyano-derivatives by the action of potassium cyanide dissolved in alcohols: this reaction appears to require the presence of a very mobile nitro-group. Examples of the second type of reaction are the conversion of para- and meta-halogenated nitrobenzenes into meta- and ortho-halogenated benzoic acids respectively, the formation of *o*-alkoxynitrobenzonitriles from *m*-dinitrobenzene (Abstr., 1885, 656), the production of chloronitrocyanoethoxybenzene from 1-chloro-2 : 4-dinitrobenzene (Van Heteren, Abstr., 1901, i, 460), and the formation of the purpuric acids from nitrophenols. The author agrees with Borsche that *iso*purpuric acid may contain the group NH·OH, but suggests that there is also present a nitro- and a nitroso-group.

The formation of 2 : 6-dinitro-3-aminophenol from 2 : 4-dinitroaniline (Lippmann and Fleissner, Abstr., 1886, 791) by the action of potassium cyanide is explained by assuming that 2 : 6-dinitro-3-aminobenzonitrile is first formed, the cyanogen group being eventually replaced by a hydroxyl group.

It is suggested that the first step in these reactions is the assumption of a molecule of potassium cyanide by a nitro-group with the formation of a compound of the nitro-acid type (Hantzsch and Kissel, Abstr., 1900, i, 89), in which the cyanogen radicle is joined to the nitrogen atom. Such a compound naturally lends itself to intramolecular transposition, the cyanogen group passing to a neighbouring ortho-position, the residual nitro group being disposed of in the various ways mentioned in the examples already quoted. These reactions do not take place unless there are replaceable hydrogen atoms in the ortho-positions to the nitro-group, and unless there is at least one other negative group (a nitro-group or a haloid atom ; a hydroxyl group is insufficient) attached to the nucleus. T. A. H.

Condensation of Aromatic Nitro-compounds with Compounds containing Reactive Methylene Groups. ARNOLD REISSERT (*Ber.*, 1904, 37, 831—838).—The addition of certain aldehydes and ketones, or of ethyl malonate, ethyl cyanoacetate, &c., to aromatic nitro-compounds in presence of aqueous or alcoholic alkali hydroxides produces intense blue or violet colorations, passing rapidly into red or brown. Acids precipitate brown condensation-products, which, however, prove to be uncrystallisable.

Nitrobenzene, acetone, and sodium methoxide react together vigorously on warming. After removal of aniline and azobenzene by distillation with steam and filtration from tarry products, hydrochloric acid precipitates a brown acid substance, and a second, lighter coloured compound, separates from the filtrate on cooling. Bromine water precipitates tribromoanilinoacetic acid from the solution.

m-Dinitrobenzene, acetone, and sodium ethoxide yield a brown acid compound according to the equation $C_6H_4(NO_2)_2 + CH_3{\cdot}CO{\cdot}CH_3 = C_9H_6O_3N_2 + 2H_2O$. An analysis of the barium salt, however, shows that the formula of the acid is probably $(C_9H_6O_3N_2)_5$.

1 : 5- and 1 : 8-Dinitronaphthalenes form similar compounds. 2 : 4-Dinitrophenol and acetone form a red, crystalline sodium salt, yielding a very unstable, violet solution on addition of acetic acid. *m*-Dinitro-

benzene and benzyl cyanide react in presence of sodium ethoxide according to the equation $2C_6H_4O_4N_2 + 2C_8H_7N = C_{28}H_{20}O_7N_6 + H_2O$. The reddish-brown acid sinters at 50° and decomposes at about 97°, and dissolves readily in alcohol, acetic acid, or chloroform, sparingly in water. C. H. D.

Preparation of Chlorinated Toluene-ω-sulphonic Acids. FARBWERKE VORM MEISTER, LUCIUS, & BRÜNING (D.R.-P. 146946).—Chlorine reacts with aqueous solutions of sodium toluene-ω-sulphonate and its derivatives, causing substitution in the benzene ring. The sulpho-group is not eliminated, as is the case with benzenesulphonic acids. Thus chlorine precipitates a mixture of sodium *o*- and *p*-chlorotoluene-ω-sulphonates from a cold solution of sodium toluene-ω-sulphonate. The two acids are separated by fractional crystallisation of their aniline salts. The *p*-salt is the more sparingly soluble, and forms flat needles melting above 260°; the *o*-salt is more readily soluble, and forms long needles melting at 249°. The action of chlorine on sodium toluene-ω-sulphonate at 100° produces a mixture of 2 : 4-, 2 : 5-, and 3 : 4-dichlorotoluene-ω-sulphonic acids. Sodium *o*-chlorotoluene-ω-sulphonate and chlorine at 100° form 2 : 5-dichlorotoluene-ω-sulphonic acid, the *p*-salt forms 2 : 4 : 5-trichlorotoluene-ω-sulphonic acid.

C. H. D.

Phenylacenaphthylmethane. CHARLES DZIEWONSKI and ELIGIO DOTTA (*Bull. Soc. chim.*, 1904, [iii], 31, 373—381. Compare Abstr., 1903, i, 431, and this vol., i, 84).—When a mixture of acenaphthene, benzyl chloride, and powdered zinc chloride is warmed first at 125° and, after the action has moderated, at 160—180° for two hours, *phenylacenaphthylmethane*, $CH_2Ph\cdot C_{10}H_5<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, is produced. This is isolated by distilling the reaction mixture and fractionating that portion of the distillate which boils from 320—360°. It crystallises from boiling alcohol in silky, white needles, melts at 112—113°, boils from 340—345°, and is soluble in ether or benzene. The *picric acid* compound is red and very unstable.

On oxidation in acetic acid solution at 85° with sodium dichromate, phenylacenaphthylmethane furnishes a mixture of *benzylnaphthalic acid*, $CH_2Ph\cdot C_{10}H_5(CO_2H)_2$, and *benzoylnaphthalic acid*,

$$COPh\cdot C_{10}H_5(CO_2H)_2.$$

The *anhydride* of the first of these can be prepared by heating the mixture of acid and anhydride first isolated at 160—165°; it crystallises from boiling acetic acid and melts at 175°. The *imide*,

$$CH_2Ph<\begin{matrix}CO\\CO\end{matrix}>NH,$$

forms yellow needles and melts at 227°.

The *anhydride* of benzoylnaphthalic acid is almost insoluble in boiling alcohol, crystallises from acetic acid in prisms, and melts at 196°; the *oxime* is deposited from solutions in acetic acid as yellow prisms and melts and decomposes at 242°; the *imide* separates from acetic acid or boiling benzene in needles and melts at 252°. It is

impossible at present to say whether this acid is identical or not with the 4-benzoylnaphthalic acid described by Graebe and Haas (Abstr., 1903, i, 409). T. A. H.

Nitration of Anthracene. JAKOB MEISENHEIMER and EDMUND CONNERADE (*Annalen*, 1904, 330, 133—184. Compare Abstr., 1901, i, 135; 1902, i, 795).—A further study has been made of the nitration of anthracene under a variety of conditions, and much of the work of Liebermann and Lindemann (Abstr., 1881, 99) and Liebermann and Landshoff (Abstr., 1881, 606) and of A. G. Perkin and Mackenzie (Trans., 1891, 59, 634; 1892, 61, 854) has been repeated. It has been found that the substances described by Liebermann and his collaborators were in many cases mixtures, and that the constitution assigned to them was not in accord with the results of the renewed investigation.

When concentrated nitric acid is added to a solution of anthracene in acetic acid, and water slowly poured into the cooled mixture, a semi-solid mass separates, from which, by dissolving in ether, *nitrodihydroanthranyl acetate*, $OAc\cdot CH<{C_6H_4 \atop C_6H_4}>CH\cdot NO_2$ (compare Dimroth, Abstr., 1901, i, 197), separates in colourless prisms melting and decomposing at 120°. It is thought that this substance is formed from the nitroanthranol, $OH\cdot CH<{C_6H_4 \atop C_6H_4}>CH\cdot NO_2$, which is first produced by addition of nitric acid to the anthracene. This anthranol can be esterified by a variety of acids. Thus, when nitrous fumes are led into a solution of anthracene in a mixture of acetic and nitric acids, *nitrodihydroanthranyl nitrite*, $NO_2\cdot CH<{C_6H_4 \atop C_6H_4}>CH\cdot NO_2$, separates as colourless needles melting and decomposing at 125°. This substance is also obtained from the acetate by the action of nitrous fumes on its solution in acetic acid. The acetate can also be converted into the chloride by the action of hydrochloric acid (Dimroth, *loc. cit.*). When the solution of the acetate in acetic anhydride is treated with sulphuric acid, or the acetate is heated with sodium hydroxide, it is converted into nitroanthracene (compare Dimroth, *loc. cit.*).

Nitrodihydroanthranyl nitrate is prepared by adding nitric acid to a suspension of anthracene in chloroform; the hydrocarbon dissolves, and white crystals of the nitrate separate; it melts and decomposes at 78—79°. Both the nitrate and nitrite easily pass into nitroanthrone. With methyl alcohol, they yield the methyl ether of nitrodihydroanthranol (m. p. 180°), and with ethyl alcohol the corresponding ethyl ether.

Trinitrodihydroanthracene, $NO_2\cdot CH<{C_6H_4 \atop C_6H_4}>C(NO_2)_2$, is formed, together with nitroanthrone, when a solution of anthracene in acetic and nitric acids is kept for some time; a similar mixture is obtained when nitrous fumes are passed into the methyl ether of nitrodihydroanthranol; it is probably formed in both cases by the action of nitrous fumes on nitroanthracene. It is prepared by passing nitrous fumes

into a solution of nitroanthracene in chloroform, and crystallises in colourless prisms melting and decomposing at 139—140°; by sodium hydroxide, it is quantitatively converted into dinitroanthracene (m. p. 294°) and nitrous acid, but no ready exchange of a nitro-group for methoxyl takes place under the influence of methyl alcohol.

By the action of excess of nitric acid on a solution of anthracene in acetic acid, a mixture of trinitrodihydroanthracene and nitroanthrone is mainly obtained, together with small quantities of dinitroanthracene and anthraquinone.

9-Nitro- and 9 : 10-dinitro-anthracenes are obtained when a solution of pure nitric acid free from nitrous acid, in acetic acid and acetic anhydride, is added to a suspension of anthracene in acetic acid at 15—20°; after 24 hours, the solid is collected and the two nitro-derivatives separated by alcohol, in which the dinitro-compound is insoluble. The mononitro-compound yields 9-aminoanthracene on reduction with stannous chloride in acetic acid solution; the *acetyl* derivative melts at 273—274°. The dinitroanthracene, which is identical with the nitrosonitroanthrone of Liebermann and Perkin, is best prepared by the action of sodium hydroxide on trinitrodihydroanthracene; on reduction, either 9-aminoanthracene or 9-aminodihydroanthracene are formed, but not the 9 : 10-diaminoanthracene. It is changed by boiling with a methyl-alcoholic solution of potassium methoxide, the *potassium* salt, $C(OMe)_2<\substack{C_6H_4 \\ C_6H_4}>C:NO\cdot OK$, being formed, since when sodium hypobromite is added to the solution, bromonitroanthrone dimethylacetal (m. p. 139°) is obtained.

By the action of nitric acid on dihydroanthracene, Liebermann and Landshoff (*loc. cit.*) obtained a dihydroanthracene nitrite; it is, however, now found that this material is a mixture of trinitrodihydroanthracene and nitroanthrone; by alkali hydroxides, the former is converted into dinitroanthracene.

All attempts to prepare Liebermann and Lindemann's "anthracene nitrite" and "hyponitrate" by the action of nitrous fumes on a chloroform solution or suspension of anthracene were unsuccessful; it appears that these authors obtained impure nitrodihydroanthranyl nitrite, but the only substance which was isolated was dinitrodihydroanthracene, $NO_2\cdot CH<\substack{C_6H_4 \\ C_6H_4}>CH\cdot NO_2$; it is sparingly soluble and melts at 194°, and is immediately converted by aqueous sodium hydroxide into nitroanthracene.

The action of nitric acid on ethyldihydroanthracene is analogous to its action on anthracene; in this case, nitroethyldihydroanthranol, the homologue of the unknown nitrodihydroanthranol, can be isolated. When ethyldihydroanthracene in solution in acetic acid is treated with nitric acid, a mixture of trinitroethyldihydroanthracene and nitroethyldihydroanthracene are formed; benzene extracts the trinitro-derivative from the mixture; the mononitro-derivative crystallises in long, colourless prisms melting and decomposing at 166°; it is soluble in alkali hydroxides, but by mineral acids it is converted into nitroethylanthracene, which appears to be identical with Liebermann and Landshoff's nitrosoethylanthrone; it crystallises in yellow prisms melt-

ing at 135°, and is readily reduced in alcoholic solution by zinc dust and ammonium chloride to the corresponding base, which, however, is unstable and was isolated as the *acetyl* derivative; the latter forms pale yellow needles melting at 259—260°.

The trinitroethyldihydroanthracene, obtained by Liebermann and Landshoff from ethyldihydroanthracene, can more easily be prepared by passing nitrous fumes into an ethereal solution of nitroethylanthracene. Nitroethylanthrone was found in the mother liquors in the nitration; it was also found by Liebermann and Landshoff.

Nitroanthrone (Perkin and Mackenzie, *loc. cit.*) cannot be acetylated; under the influence of alkalis, it is converted into the salts of iso*nitroanthrone*, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C:NO\cdot OH$, which is prepared by adding dilute sulphuric acid to an ice-cold solution of the sodium salt; it crystallises in scarlet needles, which begin to decompose at 70°, and at 80—85° has completely changed into the colourless nitroanthrone (m. p. 135°), a small quantity of anthraquinone being at the same time formed; it is stable in the dark, but in contact with water or acids rapidly changes into nitroanthrone. The *sodium* salt, prepared by dissolving nitroanthrone in hot concentrated sodium carbonate, crystallises in deep red leaflets, which rapidly decompose in moist air. The *silver* salt is a very unstable orange-red powder, which reacts quickly with methyl iodide, but no methyl derivative could be isolated. *Bromonitroanthrone*, $NO_2\cdot CBr<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CO$, is obtained when sodium hypobromite is added to a solution of the sodium salt, and forms colourless crystals melting and decomposing at 116°.

It is noteworthy that all compounds of the type of nitro-, dinitro-, nitroethyl-anthracene are intensely yellow, whilst those of the type of bromonitroanthrone are colourless and compounds of the type of *iso*nitroanthrone are red.

All attempts to obtain the methyl ether of aminoanthranol by reducing the corresponding nitro-compound were unsuccessful; a very unstable basic substance was alone formed when zinc in the presence of ammonium chloride was the agent; stannous chloride lead to the formation of anthranol.

Nitroanthrone dimethylacetal, $NO_2\cdot CH<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C(OMe)_2$, is prepared by dissolving the methyl ether of nitroanthranol in a concentrated solution of potassium methoxide in methyl alcohol, and then carefully acidifying with acetic acid, when the acetal separates; it crystallises in colourless needles melting and decomposing at 135°, and is generally contained in crude nitroanthranol methyl ether. K. J. P. O.

Preparation of *p*-Nitroaniline. THE CLAYTON ANILINE CO. (D.R.-P. 148749).—*p*-Nitroaniline is readily prepared in a pure condition by heating *p*-chloronitrobenzene with an excess of ammonia at 130—180°, the lower temperature being sufficient when a large excess of ammonia is employed. The yield is quantitative. The reaction is hastened by the use of dilute alcohol in place of water as a solvent.

C. H. D.

Equivalence of Positions 2 and 6 in the Benzene Nucleus. Emilio Noelting (*Ber.*, 1904, **37**, 1015—1028).—The equivalence of positions 2 and 6 in the benzene nucleus is shown by the following five series of experiments.

I. 6-Nitro-2-aminotoluene is converted into 2-chloro-6-nitrotoluene (Green and Lawson, Trans., 1891, **59**, 1013), which, on reduction, yields 2-chloro-6-aminotoluene (Wynne and Greeves, Proc., 1895, **11**, 151), convertible by the diazo-reaction into *2-chloro-6-hydroxytoluene*, crystallising from water in long, white needles and melting at 86°. The same compound is obtained by converting 6-nitro-2-aminotoluene into Ullmann's 6-nitro-2-hydroxytoluene and 6-amino-2-hydroxytoluene (Abstr., 1884, 1316) and treating the latter with nitrous acid and cuprous chloride. Both products were identified by their giving on nitration the same mixture of *2-chloro 5-nitro-6-hydroxytoluene* melting at 64·5° and *2-chloro-3-nitro 6-hydroxytoluene* melting at 135°. The former of these is volatile with steam and crystallises from alcohol; the latter is non-volatile and crystallises from water.

II. *2-Bromo-6-nitrotoluene*, obtained from 6-nitro-*o*-toluidine by the diazo-reaction, crystallises from alcohol in yellowish-white needles, melts at 41°, and on reduction gives *2-bromo-6-aminotoluene* as a yellow oil boiling at 253—255°; the *acetyl* derivative forms white needles melting at 158°, and the *sulphate* melts at 256°. The bromotoluidine is converted by diazotisation into *2-bromo-6-hydroxytoluene*, which crystallises from water in long, white needles, melts at 95°, and gives a *benzoyl* derivative melting at 76°; the azo-compound, prepared by interaction with diazotised *p*-nitroaniline, melts at 215°. On nitration, 2-bromo-6-hydroxytoluene gives a mixture of *2-bromo-5-nitro-6-hydroxytoluene* melting at 64° and *2-bromo-3 nitro-6-hydroxytoluene* melting at 145·5°. *6-Bromo-2-hydroxytoluene*, prepared by the diazo-reaction from 6-amino-*o* cresol, obtained by the reduction of 6-nitro-*o*-cresol, is identical in every respect with the 2-bromo-6-hydroxytoluene already described, and gives the same products of nitration.

III. *2-Iodo-6-nitrotoluene*, prepared from 6-nitro-*o*-toluidine, separates from ether in thick, yellowish-white crystals, melts at 35·5°, and on reduction gives *2-iodo-6-aminotoluene* as a colourless oil; the *hydrochloride* melts and decomposes at 254°, and the *acetyl* derivative forms white needles melting at 166°. *2-Iodo-6-hydroxytoluene* is volatile with steam, crystallises in long, silky needles melting at 90°, and is identical with the substance obtained from 6-amino-2-hydroxytoluene.

IV. *6-Nitro-2-cyanotoluene* separates from alcohol in white crystals and melts at 69·5°; *6-amino-2-cyanotoluene* crystallises from water in white needles and melts at 95·5°. *6-Chloro-2-cyanotoluene* melts at 19°, boils at 107° under 28 mm. pressure, and on hydrolysis gives *6-chloro-o-toluic acid*, which crystallises from alcohol in slender needles and melts at 159°. *2-Chloro 6-cyanotoluene*, prepared from 2-chloro-6-toluidine, is identical with 6-chloro-2-cyanotoluene and gives the same acid on hydrolysis.

V. *2-Cyano-6-hydroxytoluene*, prepared from 2-cyano-6-aminotoluene, crystallises from water in white needles, melts at 195°, and is identical with 6-cyano-2 hydroxytoluene obtained from 6-amino-2-hydroxytoluene. W. A. D.

Aryl-substituted β-Naphthylamines and their Preparation by the Sulphite Method. HANS BUCHERER and A. STOHMANN (*Zeit. Farb. Text. Chem.*, 1904, 3, 57—62 and 77—81. Compare Abstr., 1903, i, 627).—The following compounds were prepared by dissolving the naphthol or naphthylamine derivative in a minimum of water and gradually adding the sodium hydrogen sulphite to the solution heated on a water-bath. Phenyl-β-naphthylamine is obtained from β-naphthol and aniline, but the yield is poor. 2-*Anilinonaphthalene*-6-*sulphonic acid*, prepared from aniline and β-naphthol-6-sulphonic acid, crystallises in colourless leaflets; the solubility in boiling water of the sodium salt is 1 : 22, of the *aniline* salt 1 : 20, and of the p-*toluidine* salt 1 : 65. 2-o-*Tolylaminonaphthalene*-6-*sulphonic acid*, prepared from *o*-toluidine and β-naphthol-6-sulphonic acid, forms reddish-white leaflets and is soluble in 67 parts of boiling water; the analogous p-*tolyl* derivative dissolves in 6 parts, and the m-*xylyl* derivative in 4·5 parts of boiling water. 2-p-*Hydroxyanilinonaphthalene*-6-*sulphonic acid*, prepared from *p*-aminophenol, is insoluble in boiling water; 2-p-*ethoxyanilinonaphthalene*-6-*sulphonic acid*, from *p*-phenetidine, forms brownish-red leaflets and dissolves in 50 parts of boiling water. 2-p-*Aminoanilinonaphthalene*-6-*sulphonic acid*, obtained from *p*-phenylenediamine, is a grey, crystalline powder soluble in 15 parts of boiling water; *sodium* 2-p-*sulphoanilinonaphthalene*-6-*sulphonate*, $SO_3Na \cdot C_{10}H_6 \cdot NH \cdot C_6H_4 \cdot SO_3H$, prepared from sulphanilic acid and β-naphthol-6-sulphonic acid, forms red crystals which dissolve in 3 parts of boiling water. Metanilic acid gives the analogous 2-m-*sulphoanilinonaphthalene*-6-*sulphonic acid*, soluble in 3 parts of boiling water.

2-Anilinonaphthalene-8-sulphonic acid, prepared from aniline and croceic acid, is easily soluble in water, and not sparingly so, as stated in D.R.-P. 70349. 2-p-*Tolylaminonaphthalene*-8-*sulphonic acid* forms yellowish-green crystals which dissolve in 14 parts of boiling water. 2-p-*Hydroxyanilinonaphthalene*-8-*sulphonic acid* is a crystalline powder with a solubility 1 : 15 at 100°. 2-p-*Ethoxyanilinonaphthalene*-8-*sulphonic acid* is a greenish-grey, crystalline powder soluble in 40 parts of boiling water. 2-p-*Tolylaminonaphthalene*-6 : 8-*disulphonic acid* forms greenish-yellow crystals and is extremely soluble in water.

2-Anilinonaphthalene-6-sulphonic acid was also prepared from β-naphthylamine-6-sulphonic acid and aniline. 2-*Anilino*-5-*hydroxynaphthalene*-7-*sulphonic acid*, prepared from aniline and 2-amino-5-hydroxynaphthalene-7-sulphonic acid, forms snow-white crystals. 2-*Anilino*-8-*hydroxynaphthalene*-6-*sulphonic acid*, prepared from 2-amino-8-hydroxynaphthalene-6-sulphonic acid ("γ-acid"), crystallises in white leaflets and is soluble in 35 parts of boiling, and 300 parts of cold water. 2-p-*Hydroxyanilino*-8-*hydroxynaphthalene*-6-*sulphonic acid*, obtained from "γ-acid" and *p*-aminophenol, is soluble in 24 parts of boiling water; the analogous p-*ethoxy*-derivative was prepared by using *p*-phenetidine in place of *p*-aminophenol.

When 2-hydroxynaphthalene-3-carboxylic acid is heated with aniline under the foregoing conditions, phenyl-β-naphthylamine is obtained, not its carboxylic acid; the yield is 60 per cent. of the theory, and the method is the best available for preparing the base. The same carboxylic acid, when heated with *p*-aminophenol, gives 2-p-*hydroxyanilinonaphthalene*, which crystallises from a mixture of 3 parts of

alcohol and 2 of water in silver-grey leaflets with a metallic lustre and melts at 135°. 2-Anilino-8-hydroxynaphthalene-6-sulphonic acid (*supra*) was obtained from 2 : 8-dihydroxy-6-sulphonaphthalene-3-carboxylic acid and aniline, and the analogous 2-*p*-ethoxyphenyl derivative by using *p*-phenetidine instead.

Pararosaniline 2-hydroxynaphthalene-6-sulphonate,

$$C(C_6H_4\cdot NH_2)_2{:}C_6H_4{:}NH,C_{10}H_6(SO_3H)\cdot OH,$$

prepared from β-naphthol-6-sulphonic acid and pararosaniline, forms lustrous, green crystals ; at the same time the sparingly soluble 2-*para-rosanilinonaphthalene-6-sulphonic acid*,

$$C(C_6H_4\cdot NH_2)_2{:}C_6H_4{:}N\cdot C_{10}H_6\cdot SO_3H,$$

is formed in much larger amount ; it forms dark brown crusts with a red, metallic sheen or a finely crystalline powder, and is also obtainable from β-naphthylamine-6-sulphonic acid. W. A. D.

8-Chloro-α-naphthylamine and its Sulphonic Acids. Badische Anilin- & Soda-Fabrik (D.R.-P. 147852).—The azimino-compounds obtained by the action of nitrous acid on 1 : 8-diamino-derivatives of naphthalene react readily with hydrochloric acid in presence of copper or cuprous salts, forming 8-chloro-α-naphthylamine derivatives. Hydrogen chloride is passed into a mixture of the azimino-compound with hydrochloric acid until saturated, and copper paste is then added.

8-*Chloro-α-naphthylamine-3 : 6-disulphonic acid*, from the azimino-compound of naphthylene-1 : 8-diamine-3 : 6-disulphonic acid, crystallises in slender needles ; it is diazotisable, and yields 8-amino-α-naphthol-3 : 6 disulphonic acid on fusion with an alkali hydroxide, whereas on heating with dilute sulphuric acid under pressure, it furnishes 8-chloro-α-naphthol-3 : 6-disulphonic acid, which gives rise to 1 : 8-dihydroxy-naphthalene-3 : 6-disulphonic ("chromotrope") acid when fused with an alkali hydroxide. C. H. D.

Thiodiacylanilides. George S. Jamieson (*J. Amer. Chem. Soc.*, 1904, 26, 177—183).—The compound obtained by Tschugaeff (Abstr., 1902, i, 604) by the action of potassium xanthate on benzanilidimide chloride shows no tendency to undergo molecular rearrangement and can be heated above its melting point without change. When heated with strong ammonia, it suffers decomposition with formation of thiobenzanilide and a small quantity of phenylthiourethane,

$$OEt\cdot CS\cdot NHPh.$$

If it is treated with concentrated hydrochloric acid, benzanilide is produced. It is therefore concluded that this compound has the constitution $CSPh\cdot NPh\cdot CS\cdot OEt$.

Benzoylthiobenzanilide, $CSPh\cdot NPhBz$, obtained by the interaction of potassium thiobenzoate and benzanilidimide chloride, crystallises from alcohol in bright red prisms, melts at 108—109°, and is decomposed by boiling hydrochloric acid with formation of thiobenzanilide. This compound can also be obtained by the action of benzoyl chloride on the sodium salt of thiobenzanilide.

p-*Bromobenzoylthiobenzanilide*, $CSPh\cdot NPh\cdot CO\cdot C_6H_4Br$, prepared by the action of potassium *p*-bromothiobenzoate on benzanilidimide chloride, crystallises from alcohol in slender, orange-coloured prisms and melts at 120—121°.

Benzoylthio-p-*bromobenzanilide*, $C_6H_4Br{\cdot}CS{\cdot}NPhBz$, formed by the interaction of *p*-bromobenzanilidimide chloride and potassium thiobenzoate, crystallises in slender, red prisms, melts at 133—134°, and is not changed by heating at 140° for 5 minutes. p-*Bromothiobenzanilide*, obtained from the mother-liquor from this reaction, is readily soluble in hot alcohol and melts at 161—162°.

The *compound*, $NPh{:}CPh{\cdot}N(C_7H_7){\cdot}CSPh$, obtained by the action of benzanilidimide chloride on sodium thiobenzo-*p*-toluidide, forms yellow crystals, melts at 198—201°, and is very soluble in benzene or amyl acetate. The same compound may be prepared by the action of benzoyl-*p*-toluidimide on the sodium salt of *p*-thiobenzanilide.

The *compound*, $NPh{:}CPh{\cdot}NPh{\cdot}CSPh$, formed by the interaction of benzanilidimide chloride and sodium thiobenzanilide, crystallises in yellow prisms and melts at 202—204°. E. G.

Action of Silver Cyanate on Acyl Chlorides. III. Otto C. Billeter (*Ber.*, 1904, 37, 690—696. Compare Abstr., 1902, i, 821).—*Benzenesulphonecarbimide*, $C_6H_5{\cdot}SO_2{\cdot}N{:}CO$, prepared by heating together benzenesulphonic chloride and silver cyanate, is a colourless, mobile liquid which boils at 129·6° under 9 mm., at 139·4° under 13·5 mm. pressure, and does not solidify at −22°; it has a sp. gr. 1·369° at 19°/4°. It is rapidly decomposed by water, giving carbon dioxide and benzenesulphonamide; concentrated sulphuric acid gives carbon dioxide and benzenesulphonamide sulphate. Hydrogen chloride is without action, but hydrogen iodide forms an unstable *additive* compound, $SO_2Ph{\cdot}N{:}CO,HI$. Aluminium chloride in benzene solution converts the carbimide into benzoylbenzenesulphonamide,

$$C_6H_5{\cdot}SO_2{\cdot}NHBz,$$

small quantities of diphenylsulphone being also formed.

Alcohol converts the carbimide into *ethyl benzenesulphonylcarbamate*, $SO_2Ph{\cdot}NH{\cdot}CO{\cdot}OEt$, which crystallises from alcohol in small plates and melts at 109°; the *sodium* salt, $SO_2Ph{\cdot}NNa{\cdot}CO_2Et$, is crystalline. *Phenyl benzenesulphonylcarbamate*, $SO_2Ph{\cdot}NH{\cdot}CO_2Ph$, prepared by the interaction of the carbimide with phenol, crystallises from water and melts at 123°. With ammonia, *benzenesulphonylcarbamide*, $SO_2Ph{\cdot}NH{\cdot}CO{\cdot}NH_2$, is obtained; it crystallises in felted, hair-like needles melting at 167·4°. With aniline, the *compound*

$$SO_2Ph{\cdot}NH{\cdot}CO{\cdot}NHPh$$

is obtained as a crystalline powder melting at 158·4°; the *compound* $SO_2Ph{\cdot}NH{\cdot}CO{\cdot}NPhEt$, prepared from ethylaniline, melts at 123·2°.

Benzenesulphonylacetylcarbamide, $SO_2Ph{\cdot}NH{\cdot}CO{\cdot}NHAc$, prepared from acetamide, forms small plates and melts at 155—156°; the analogous *benzenesulphonylbenzoylcarbamide*, obtained from benzamide, forms silky needles and melts at 208°. *Dibenzenesulphonylcarbamide*, $CO(NH{\cdot}SO_2Ph)_2$, prepared from benzenesulphonamide, crystallises from alcohol in long, colourless prisms and melts at 159°. W. A. D.

Behaviour of Salol and Betol towards Various Solvents. Valerio Lusini (*L'Orosi*, 1903, 26, 80—85).—Salol is soluble in methyl, ethyl, *n*-propyl, butyl, or amyl alcohol, amylene hydrate, ethylene glycol, mannitol, ether, light petroleum, chloroform, benzene, carbon

disulphide, acetaldehyde, methylal, acetal, or acetone; it dissolves only slightly in glycerol, whether concentrated or diluted with water. Its alcoholic solution gives, with ferric chloride, the violet coloration characteristic of the phenols; this reaction is also yielded by its solutions in all the above-named monohydric alcohols, and in acetal, acetaldehyde, and acetone; in the other solvents and also in water, however, the reaction is not obtained. In water containing only 0·25—0·35 per cent. of alcohol, salol shows the phenol reaction; so that, assuming the reaction to be due to the resolution of the salol, the presence in the organism of alcoholic liquors would be sufficient to bring about this resolution.

Betol (β-naphthyl salicylate) is absolutely insoluble in water, but dissolves in the monohydric alcohols named above, the solubility decreasing as the molecular weight increases; it is soluble also in acetaldehyde, ether, chloroform, benzene, carbon disulphide, &c., but does not dissolve in ethylene glycol, glycerol, or mannitol. In this case, the colorations obtained with ferric chloride are much less intense and more transitory than with salol. The reaction is fairly marked in methyl or ethyl alcohol, but diminishes in intensity for the higher alcohols; it is not shown in methylal, is scarcely apparent in acetaldehyde or acetal, but is very marked in acetone solution. In aqueous alcohol of less strength than 60 per cent., betol does not give a coloration with ferric chloride. T. H. P.

Mixtures of *o*-Nitrophenol and Naphthalene. A. V. Saposchnikoff and P. Helwig (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1084—1097).—Melting point curves and tables of mixtures of *o*-nitrophenol and naphthalene show that these compounds dissolve one another in the liquid state, but do not form solid solutions. The melting point curve consists of two parts, which meet in a eutectic point at about 29·7°, corresponding with a mixture containing 67·2 per cent. (mols.) of the nitrophenol.

On comparing the curves for mixtures of naphthalene with picric acid, 2 : 4-dinitrophenol (see two following abstracts), or *o*-nitrophenol, it is seen that a fall in the number of nitro-groups in the substituted phenol shows itself in the character of the diagram obtained. The formation of a molecular compound of naphthalene and 2 : 4-dinitrophenol is not so clearly indicated in the melting point curve as in the case of picric acid. T. H. P.

Mixtures of 2 : 4-Dinitrophenol and Naphthalene. A. V. Saposchnikoff and P. Helwig (*J. Russ. Phys. Chem. Soc.*, 1903, 35, 1075—1084).—The melting point diagrams and tables for mixtures of 2 : 4-dinitrophenol and naphthalene show that these substances unite in molecular proportions to form a compound which melts at 91·7°; this melting point is lowered by the addition of either of the constituent compounds. Besides the first solidifying point, all mixtures of 2 : 4-dinitrophenol and naphthalene have a second, which is that of complete solidification, and has the same value for mixtures containing the same proportion more or less than 50 per cent. (mols.) of the dinitrophenol; hence these compounds do not form solid solutions, but, from molten mixtures of them, the constituent which is present in

excess first crystallises out, and, when the liquid has reached the eutectic composition, crystallisation of the second constituent begins.

T. H. P.

Mixtures of Picric Acid and Naphthalene. A. V. SAPOSCHNIKOFF AND W. RDULTOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1073—1074).—The authors have determined the melting point curve of mixtures of picric acid and naphthalene. Starting from 80°, the melting point of pure naphthalene, the curve falls to a eutectic point 77·5° for a mixture containing 12·3 per cent. (mols.) of picric acid; it then rises continuously to 149·5°, when the mass contains molecular proportions of the two constituents. After this it falls to another eutectic point, 115°, the percentage (mols.) of naphthalene being then 8·59; finally, it rises to 122·5°, the melting point of picric acid. A molecular compound, melting at 149·5°, of naphthalene and picric acid is thus formed, and this may be also obtained by mixing the two constituents in molecular proportions in alcoholic solution. The points 77·5° and 115° correspond with eutectic mixtures of the molecular compound and naphthalene and picric acid respectively.

T. H. P.

[4-Chloro-2-aminophenolsulphonic Acid.] AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 148198).—Sodium hydrogen sulphite converts 4-chloro-2-nitrophenol into 4-*chloro*-2-*aminophenolsulphonic acid*, crystallising in slender, transparent, prismatic needles. It is isomeric with the acid obtained on sulphonating 4-chloro-2-aminophenol, which is more readily soluble in water and crystallises in felted aggregates at the surface of the solution. The acid prepared by means of sulphite forms soluble azo-compounds when diazotised and combined with 8-amino-α-naphthol-2 : 4- or -3 : 6-disulphonic acid.

C. H. D.

Mixtures of Trinitrocresol and Naphthalene. A. V. SAPOSCHNIKOFF AND W. RDULTOWSKY (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1097—1098).—Mixtures of trinitrocresol and naphthalene give a melting point curve similar to that obtained with picric acid and naphthalene. The molecular compound formed, which melts at 124·5°, may also be prepared by mixing the constituents in alcoholic solution.

T. H. P.

Derivatives of Safrole, and its Relations to the Phenol Ethers, Eugenole and Asarone. HERMANN THOMS and A. BLITZ (*Arch. Pharm.*, 1904, **242**, 85—94. Compare Abstr., 1903, i, 415, 558; 1904, i, 47).—*Nitrodihydrosafrole* (6-*nitro*-3 : 4-*methylenedioxy*-1-*propylbenzene*), $NO_2\cdot C_6H_2Pr^{\alpha}\colon O_2\colon CH_2$, is obtained by adding 45 per cent. nitric acid gradually to an acetic acid solution of dihydrosafrole (Ciamician and Silber, Abstr., 1890, 966); it is yellow and melts at 36°. By treatment with aluminium chloride in the presence of carbon disulphide (Hartmann and Gattermann, Abstr., 1893, i, 152), it is converted into 6-*nitro*-3 : 4-*dihydroxy*-1-*propylbenzene*,

$$NO_2\cdot C_6H_2Pr^{\alpha}(OH)_2,$$

melting at 73°; this, when methylated with methyl sulphate (Ullmann, Abstr., 1900, i, 619; 1903, i, 395), gives the 6-nitro-3 : 4-dimethoxy-1-propylbenzene, melting at 81°, already described (Abstr., 1903, i, 415). The position of the nitro-group is thus established. When the last substance is hydrolysed by means of aluminium chloride, two products are obtained. One melts at 52°, and, when heated at 130° with ethyl iodide, gives a yellow *derivative* melting at 60°; this, on reduction with amalgamated aluminium, yielded an amine, by the oxidation of which with sodium dichromate and dilute sulphuric acid at 0° a quinone melting at 111°, already described (Abstr., 1903, i, 416), was obtained: the product melting at 52° is thus 6-*nitro*-3-*hydroxy*-4-*methoxy*-1-*propylbenzene*, $NO_2 \cdot C_6H_2Pr^{\alpha}(OMe) \cdot OH$. The second product melts at 78° and has the composition $C_{10}H_{13}O_4N,H_2O$; with ethyl iodide, it forms a *derivative* melting at 76°; it is presumably the 4-*hydroxy*-3-*methoxy*-isomeride of the other product.

Nitrodihydrosafrole is reduced by amalgamated aluminium (H. Wislicenus, Abstr., 1896, i, 671) to *aminodihydrosafrole* (6-*amino*-3 : 4-*methylendioxy*-1-*propylbenzene*); this is an unstable substance, melting at 24° and boiling at 156° under 11·5 mm. pressure; its *hydrochloride* melts and decomposes above 200°; its *acetyl* derivative, prepared by means of thioacetic acid (Pawlewski, Abstr., 1898, i, 362; 1902, i, 209), melts at 171·5°, its *benzoyl* derivative at 151°; by the diazo-reaction, it can be converted into 6-*hydroxy*-3 : 4-*methylenedioxy*-1-*propylbenzene*, which melts at 71—72°.

Fuming nitric acid at 20° converts nitrodihydrosafrole into *di*- (not tri-) *nitrodihydrosafrole* (2 : 6-*dinitro*-3 : 4-*methylenedioxy*-1-*propylbenzene*); this is yellow and melts at 121°. It is reduced by amalgamated aluminium to *diaminodihydrosafrole* (2 : 6-*diamino*-3 : 4-*methylenedioxy*-1-*propylbenzene*), which melts at 72°; the (mono)*hydrochloride* of this melts and decomposes at 246°, the *benzoyl* derivative melts at 248°; with nitrous acid, a brown dye is formed (meta-position of the two amino-groups). Alcoholic ammonium sulphide effects a reduction to an orange-red *nitroaminodihydrosafrole* melting at 76·5°, which, when the NH_2 is replaced by hydrogen by diazotisation in boiling alcoholic solution, gives the 2-nitro-compound melting at 36° described above, and so must be 6-*nitro*-2-*amino*-3 : 4-*methylenedioxy*-1-*propylbenzene*.

C. F. B.

Properties of Phenyl Ether. ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1904, 26, 302—304).—Phenyl ether crystallises in large prisms or thin, white plates, melts at 26·9—27°, boils at 258·97° (corr.), and is soluble in all the usual organic solvents and slightly so in water. It dissolves to the extent of 4·9 parts in 100 parts of 87 per cent. alcohol at −10°, and is much more soluble at higher temperatures. It volatilises slowly at the ordinary temperature and more rapidly when heated. The sp. gr. of the liquid ether is 1·0535 at 40°; 1·0582 at 35°; 1·0629 at 30°; 1·0677 at 25°; 1·0724 at 20°; and 1·0773 at 15°. The solid ether has a sp. gr. 1·1508 at 10·75°. The pure substance is not affected by light, but, if impure, it gradually assumes a deep yellow colour.

E. G.

Behaviour of Phenol Ethers on Distillation with Zinc Dust. HERMANN THOMS (*Arch. Pharm.*, 1904, **242**, 95—98).—Contrary to the opinion usually held, anisole (methoxybenzene) is decomposed in part when it is mixed with zinc dust and distilled. In all, 60 grams of anisole were distilled in portions of 2·5 grams; ethylene was formed, and 20 grams of liquid distillate were obtained, from which about 3 grams each of benzene and phenol, 2·5 grams of diphenyl, and 10 c.c. of unchanged anisole were isolated. C. F. B.

Preparation of Ethers by means of Magnesium Compounds and Halogen Methyl Ethers, XCH_2OR. JULES HAMONET (*Compt. rend.*, 1904, **138**, 813—814).—By a modification of Henry's method for preparing ethers from halogen methyl ethers (compare Henry, Abstr., 1892, 27), namely, the substitution of Grignard's organo-magnesium compounds for the organo-zinc compounds, the author has obtained a better yield of the ether, 60—65 per cent. of the theoretical in the case of the open chain compounds, but much less in the case of the ring compounds. The reaction, which is represented by the equation $RMgX + XCH_2 \cdot OR = MgX_2 + CH_2R \cdot OR$, proceeds more readily with the bromo-derivative of the methyl ether than with the chloro- or iodo-compound, and the bromomethyl ethers are prepared by the action of hydrobromic acid on the corresponding chloro-compounds. The action of bromomethyl ether, $CH_2Br \cdot OMe$, and bromomethyl amyl ether, $CH_2Br \cdot O \cdot C_5H_{11}$ (a liquid boiling at 74—76° under 18 mm. pressure), on the magnesium derivatives of ethyl bromide, phenyl bromide, and benzyl chloride was studied, and the following ethers were prepared: propyl amyl ether, $C_3H_7 \cdot O \cdot C_5H_{11}$, boiling at 130°, benzyl methyl ether, $CH_2Ph \cdot OMe$, boiling at 170°, and *phenylethyl methyl* ether, $OMe \cdot CH_2 \cdot CH_2Ph$, a colourless liquid boiling at 189—190°. M. A. W.

Action of Bromine and Chlorine on Phenols: Substitution Products, ψ-Bromides, and ψ-Chlorides. X. Action of Bromine on *p*-Dihydroxydiphenylmethane. THEODOR ZINCKE and R. KRÜGENER (*Annalen*, 1903, **330**, 61—81).—Tetrabromo-*p*-dihydroxydiphenylmethane is readily prepared by treating dihydroxydiphenylmethane in acetic acid solution with bromine (compare Staedel, Abstr., 1878, 420); it melts at 226—227°, and yields an *acetyl* derivative when acted on with acetic anhydride in the presence of sulphuric acid, which crystallises in needles melting at 167—168°. When the tetrabromide is left in contact with bromine for 24 hours, a *hexabromide*, $CH_2\left(C{<}{\begin{smallmatrix}CH{=}CBr\\CBr{\cdot}CBr\end{smallmatrix}}{>}C{\cdot}OH\right)_2$, is formed, which crystallises in colourless needles melting at 204°, and is not acted on by reducing agents or by sodium methoxide; its *diacetyl* derivative crystallises in needles melting at 215°.

*ψ-Heptabromo-*p*-dihydroxydiphenylmethane*,

$$CHBr\left(C{<}{\begin{smallmatrix}CH{-}CBr\\CBr{:}CBr\end{smallmatrix}}{>}C{\cdot}OH\right)_2$$

or $CO<\begin{matrix}CBr{=}CH\\CBr{:}CBr\end{matrix}>CH\cdot CHBr\cdot C<\begin{matrix}CH{-}CBr\\CBr{:}CBr\end{matrix}>C\cdot OH$, prepared by heating the hexabromide with excess of bromine under pressure at 100° for four hours, is purified by recrystallising from acetic acid containing hydrogen bromide, from which it separates in colourless needles or prisms melting and decomposing at 205—206°, the prismatic form showing signs of change at a lower temperature, 194°. Under a great variety of conditions, treatment with moist ether, methyl or ethyl alcohol, acetone, with aqueous sodium carbonate or acetate, with strips of various metals, zinc, &c., and with sulphuric acid, it loses hydrogen bromide, yielding a benzylidenequinone. By hydriodic acid, it is converted into hexabromodihydroxydiphenylmethane. When boiled with acetic anhydride, the ψ-bromide is converted into *diacetoxyhexabromo-p diphenylbromomethane*, $CHBr(C_6HBr_3\cdot OAc)$, which crystallises in colourless needles melting at 227—228°.

Hexabromohydroxybenzylidenequinone,

$$CO<\begin{matrix}CBr{:}CBr\\CBr{=}CH\end{matrix}>C{:}CH\cdot C<\begin{matrix}CH{-}CBr\\CBr{:}CBr\end{matrix}>C\cdot OH,$$

is best prepared by dissolving the ψ-heptabromide in aqueous acetone, when the solution becomes deeply coloured and a mass of crystals separates; it crystallises in small, red needles melting at 245°, and is relatively stable; it dissolves in sulphuric with a violet coloration, and readily forms additive products with hydrogen chloride and bromide, in the latter case forming the ψ-heptabromide, and in the former a *ψ-hexabromochloro*-compound, which crystallises in needles, melting and decomposing at 215—217°. When reduced with hydriodic acid, hexabromodihydroxydiphenylmethane is produced. It forms a series of salts which dissolve with a blue colour; the *sodium* salt is prepared by treating an acetone solution of the heptabromide with sodium carbonate and crystallises in bluish-violet metallic needles or leaflets; it is decomposed by the same agents which attack the quinone. Other salts can be prepared by precipitation from the sodium salt. Further, when strips of zinc or magnesium are immersed in an ethereal solution of the heptabromide, they become covered with crystals of the corresponding salts of the two metals.

Hexabromodihydroxydiphenylhydroxymethane,

$$OH\cdot CH\left(C<\begin{matrix}CBr{:}CBr\\CH{-}CBr\end{matrix}>C\cdot OH\right)_2,$$

is prepared by adding only so much water to an acetone solution of the heptabromide that the quinone is not precipitated; the original deep colour slowly disappears, and on diluting the new substance separates; it can also be obtained from the mother liquor from the preparation of the quinone; it crystallises in rhombic plates, melting and decomposing at 250°, and in slender needles melting and decomposing at 247°. It is converted by dissolution in sulphuric acid into the quinone. Its *triacetyl* derivative, which can be prepared either from the hydroxymethane or by treating the quinone with acetic anhydride and sulphuric acid, forms lustrous needles melting at 204°. Evidence of the existence of the quinonoid form of the carbinol was obtained; it forms a deep violet solution in alkali carbonates, which is rapidly decolorised by the air.

Hexabromodihydroxydiphenylmethoxymethane,
$OMe\cdot CH(C_6HBr_3\cdot OH)_2$,
prepared by treating the heptabromide with methyl alcohol, or by warming a solution of the quinone in methyl alcohol, forms colourless, monoclinic crystals melting and decomposing at 179°. The corresponding *ethoxy*-derivative is obtained in a similar manner, and forms rhombic crystals melting at 189—190°. *Hexabromodihydroxydiphenylacetoxymethane*, produced when either the heptabromide or the quinone is treated with acetic acid, forms small crystals, melting and decomposing at 225—226°; another form crystallising in needles begins to melt at 208°. With alkalis, it is converted into salts of the quinone.

K. J. P. O.

Methylene Compounds of the Phloroglucinol Series. RUDOLF BOEHM (*Annalen*, 1903, 329, 269—331. Compare Abstr., 1902, i, 37).—Most members of the phloroglucinol series yield, more or less readily, methylene derivatives with formaldehyde; the following substances have been investigated: phloroglucinol and its monomethyl ether, cotoin, methylphloroglucinol and its β-monomethyl ether, aspidinol (the β-methyl ether of methylphloroglucinyl-*n*-butanone), and filicic acid. 1:3:5-Trimethylphloroglucinol will not react with formaldehyde, even at a high temperature in the presence of a condensing agent. The presence of methyl groups in the nucleus increases the ease with which phloroglucinols react with formaldehyde. In the case of the monomethyl ethers of phloroglucinol, the methylene group takes up an ortho-position relatively to the methoxy-group.

Phloroglucinol and methylphloroglucinol (that is, compounds with two CH groups) yield complex dimolecular or trimolecular methylene compounds, which are unstable, and obtained crystalline only with difficulty. Those derivatives of phloroglucinol which contain only one CH group, dimethylphloroglucinol, aspidinol, and filicyl-*n*-butanone, yield well crystalline and stable methylene derivatives. From phloroglucinol, red, amorphous compounds are obtained which are insoluble in acids and alkalis. In the case of monomethyl ethers, even when two CH groups are present, only simple condensation products are formed.

The methylene derivatives are decomposed by sodium hydroxide and zinc dust into two or four homologous phloroglucinols, according to their complexity, amorphous by-products being produced in the case of secondary phloroglucinols.

According to their behaviour with alcoholic diazoaminobenzene, these methylene compounds fall into three groups: (1) the derivatives of methylphloroglucinol and its β-monomethyl ether, and filicic acid (that is, compounds having one CH group in the nucleus), yield with two mols. of diazoaminobenzene well crystallised azo-compounds with two azo-groups corresponding with the diphenylmethane type. Further treatment with alcoholic diazoaminobenzene effects cleavage at the methylene bridge and formation of a disazo-compound. (2) Methylene derivatives which do not contain a CH group in the nucleus, such as the derivatives of dimethylphorogluciuol and filicyl-*n*-butanone, are directly decomposed, benzeneazophloroglucinols being produced.

Flavaspidic and filicic acids and albaspidin and phloraspin belong to this group. (3) Methylene derivatives not containing a CH group, and with methoxy-groups in the ortho-position relatively to the methylene group, do not react with diazoaminobenzene; to this group belongs the natural aspidin.

Phloroglucinol does not react with formaldehyde at the ordinary temperature in aqueous solution, but in the presence of 15 per cent. sulphuric or hydrochloric acids a reaction takes place, crystals rapidly separating; these crystals are not permanent. In order to obtain methylenebisphloroglucinol, 2 mols. of phloroglucinol and 1 mol. of formaldehyde must be used, and the product, which contains complex substances, shaken with water, dissolved in ether, and finally precipitated from solution in ethyl acetate by benzene, the second fraction containing the methylene derivative. Sodium hydroxide and zinc dust convert the mixture of condensation products into phloroglucinol and methylphloroglucinol (about equal quantities), a very small quantity of dimethylphloroglucinol, and somewhat more trimethylphloroglucinol. Diazoaminobenzene yields an insoluble, dark red azo-compound.

The monomethyl ether of phloroglucinol cannot only be prepared synthetically, but also by treatment of cotoin with zinc dust and sodium hydroxide; with formaldehyde, the ether condenses to form methylenebisphloroglucinol methyl ether, which is decomposed by sodium hydroxide and zinc dust, producing the β-methyl ether of methylphloroglucinol (m. p. 119°). From cotoin, methylenebiscotoin, $CH_2[C_6HBz(OMe)(OH)_2]_2$ (the "fortoin" of commerce), is readily prepared; on reduction, it yields the monomethyl ethers of phloroglucinol and of methylphloroglucinol. Methylenebiscotoin is converted by diazoaminobenzene into an *azo*-compound,

$$CH_2[C_6Bz(OMe)(OH)_2 \cdot N_2Ph]_2,$$

which forms scarlet crystals melting at 246°, and is not changed by further treatment with diazoaminobenzene.

Methylphloroglucinol combines slowly with formaldehyde, but in presence of sulphuric acid it reacts very rapidly, forming a mass of minute, colourless needles, which melt and decompose at 230°; the aqueous solution of the substance, methylenebismethylphloroglucinol, gives a pale violet-red coloration with ferric chloride, and then a pale brown precipitate. On reduction, it is converted into a mixture of methyl- and dimethyl-phloroglucinols.

When methylphloroglucinol (3 mols.) is condensed with formaldehyde (2 mols.), a substance is obtained from which, on reduction, 1 : 3 : 5-trimethylphloroglucinol can be prepared.

By the action of diazoaminobenzene on methylenebismethylphloroglucinol, the *azo*-compound, $CH_2[C_6Me(OH)_3 \cdot N_2Ph]_2$, is formed; it crystallises in brownish-black needles, which are unchanged at 290°, and on further treatment with diazoaminobenzene are converted into *methylphloroglucinoldisazobenzene*, $C_6Me(OH)_3 \cdot N_2Ph$; the latter crystallises in scarlet needles and decomposes at 238°.

The β-methyl ether of methylphloroglucinol, prepared from aspidin or aspidinol, condenses readily with formaldehyde, forming the *methyl* ether of *methylenebismethylphloroglucinol*, $CH_2(C_8H_9O_3)_2$, which forms colourless crystals melting at 228—229°. On reduction, small

quantities of the β-methyl ethers of methyl- and dimethyl-phloroglucinols are obtained. With diazoaminobenzene, an *azo*-compound,

$$CH_2[C_6Me(OMe)(OH)_2\cdot N_2Ph]_2,$$

is obtained as dark red needles melting at 245—246°; with excess of diazoaminobenzene, the disazo-compound, $C_6Me(OMe)(OH)_2(N_2Ph)_2$, melting at 204°, is formed.

Methylenebisaspidinol, $C_{25}H_{32}O_8$, is obtained by the action of formaldehyde on an aqueous alcoholic solution of aspidinol (the β-methyl ether of methylphloroglucinol-*n*-butanone), and crystallises in colourless prisms melting at 190—191°, and gives a green coloration with ferric chloride in alcoholic solution. On reduction, the β-methyl ethers of methyl- and dimethyl-phloroglucinols are formed: from the formation of the last-named ether, it follows that aspidinol is represented by the formula $OMe\cdot C{<}\begin{matrix}CMe{:}C(OH)\\CH-C(OH)\end{matrix}{>}C\cdot COPr^{\alpha}$.

Filicic acid (dimethylphloroglucinol) reacts with formaldehyde only in alkaline solution, the methylene derivative, $CH_2(C_8H_9O_3)_2$, being produced; it is a colourless, amorphous powder, softening at 150° and forming a liquid above 200°. On reduction with sodium hydroxide and zinc dust, besides filicic acid, methylfilicic acid (1 : 1 : 3-trimethylphloroglucinol) is obtained, crystallising in colourless needles or prisms, which melt at 178—180° and soon become yellow in moist air. In aqueous solution, it gives with ferric chloride a reddish-violet coloration, which changes to yellow, whilst a yellow precipitate separates. Ammoniacal silver nitrate is immediately reduced in the cold. Methylfilicic acid is less reactive than the parent substance, and does not yield crystalline derivatives with phosphorus pentachloride, acetyl chloride, or benzoyl chloride. When submitted to the action of bromine in acetic acid solution, a *dibromomethylfilicic acid*, $C_9H_{10}O_3Br_2$, is obtained, crystallising in colourless prisms melting at 142°. With excess of bromine in the presence of water, a keto-bromide, *tribromomethylfilicic acid*, $CO{<}\begin{matrix}CMe_2\cdot CO\\CBr_2-CO\end{matrix}{>}CMeBr$, is formed; it crystallises in colourless needles, melting at 116°, decomposes potassium iodide, and gives no reaction with ferric chloride. By bromine and alkalis, it is profoundly changed, bromoform, carbon tetrabromide, and dimethylmalonic acid having been isolated. It is pointed out that three formulæ are possible for methylfilicic acid, differing in the relative positions of the two hydroxyl and the keto-groups.

Methylenebisfilicic acid and diazoaminobenzene yield an *azo*-derivative, containing two benzeneazo-groups, $C_{29}H_{28}O_6N_4$, which crystallises in lemon-yellow needles melting at 223—224°; on further treatment with excess of diazoaminobenzene, decomposition takes place, *filicyldiazobenzene*, $C_6H_2Me_2O_3(N_2Ph)_2$, being obtained as dark red crystals melting at 209°. K. J. P. O.

Methylene Compounds and Two New Homologues of Orcinol.

OSCAR SIMON (*Annalen*, 1903, 329, 301—310).—The methylene compounds of orcinol are analogous to those of phloroglucinol (preceding abstract) in that they are reduced by sodium hydroxide and zinc dust

yielding derivatives of *m*-dihydroxybenzene, but they are not decomposed by diazoaminobenzene in alcoholic solution.

Methylenebisorcinol (Möhlau and Koch, Abstr., 1895, i, 46) reacts with diazoaminobenzene, forming the *azo*-compound,

$$CH_2[C_6HMe(OH)_2\cdot N_2Ph]_2,$$

which crystallises in dark red needles and is not affected by further treatment with diazoaminobenzene. Orcinol yields the *disazo*-compound, $C_6Me(OH)_2(N_2Ph)_2$, which crystallises in scarlet needles melting and decomposing at 229—230°.

When methylenebisorcinol is decomposed by sodium hydroxide and zinc dust, mol. proportions of orcinol and a dimethyldihydroxybenzene, which must be the hitherto unknown third isomeride,

$$CH{<}{\begin{matrix}C(OH){:}CMe\\C(OH){-}CH\end{matrix}}{>}CMe,$$

are formed; it follows from this fact that the methylene group is attached to the carbon atom in the ortho-position relatively to the hydroxyl group.

3 : 5-*Dihydroxy*-1 : 2-*dimethylbenzene* crystallises with $1H_2O$ in colourless prisms, melting when free from water at 136—137°; it yields an intense indigo-blue coloration with ferric chloride, and, on treatment with benzoyl chloride by the Schotten-Baumann method, forms a *dibenzoyl* derivative, which crystallises in colourless prisms melting at 100—102°. When acted on by excess of bromine in acetic acid, the phenol is converted into a *keto-bromide*, $CBr_2{<}{\begin{matrix}CO\cdot CMe\\CO\cdot CBr_2\end{matrix}}{>}CMe$, which crystallises in pale yellow, rhombic plates or prisms, melting and decomposing at 128—129°, and is decomposed by sodium hydroxide, bromoform being produced. On digesting the phenol with diazoaminobenzene in alcoholic solution, 3 : 5-*dihydroxy*-1 : 2-*dimethylbenzenedisazobenzene*,

$$C_6Me_2(OH)_2(N_2Ph)_2,$$

is formed, and crystallises in long, pale red needles melting and decomposing at 229°; from acetic acid, it crystallises with one mol. of acetic acid.

3 : 5-Dihydroxy-1 : 2-dimethylbenzene condenses with formaldehyde in the presence of sulphuric acid, forming a methylene derivative from which 4 : 6-*dihydroxy*-1 : 2 : 3-*trimethylbenzene*, $CH{<}{\begin{matrix}C(OH)\cdot CMe\\C(OH){:}CMe\end{matrix}}{>}CMe$, is obtained on reduction with sodium hydroxide and zinc dust. It crystallises in rhombic leaflets or colourless needles melting at 163—164°; the *dibenzoyl* derivative forms colourless prisms melting at 191°. The same dihydroxytrimethylbenzene is obtained on reducing the crude methylenebisorcinol, a fact which shows that this material contains at least a trimolecular condensation product. From the constitution of the dihydroxytrimethylbenzene, it follows that both the methylene groups in the trimolecular compound must be in the ortho-position relative to the methyl group of orcinol. K. J. P. O.

Flavaspidic Acid. Rudolf Boehm (*Annalen*, 1903, **329**, 310—320. Compare Abstr., 1902, i, 37).—When flavaspidic acid is reduced by digesting the acid (1 part) with a solution of hydriodic acid (2 parts) in acetic acid (10 parts), 45 per cent. of the original

material is obtained as an insoluble substance forming colourless crystals, which melt and decompose at 257—259° and become red in colour when kept. This substance appears to be formed by the opening of the four-membered ring (compare *loc. cit.*), the addition of two atoms of hydrogen, and the elimination of water, and consequently to have the formula $\begin{array}{l} CO\cdot CMe_2\text{-}C\text{—}O\text{—}C\cdot C(COPr^{\alpha})\cdot C\cdot OH \\ COPr^{\alpha}\cdot C\colon C(OH)\cdot C\cdot CH_2\cdot C\cdot C(OH)\text{——}CMe \end{array}$; this anhydride is called *dihydroflavaspidylxanthen.* By digestion with sodium hydroxide and zinc dust, one butyryl group is eliminated, and a *compound,* $C_{20}H_{22}O_6$, obtained, which, with 1 mol. of acetone, forms crystals melting at 213—215°. Unlike the anhydride containing two butyryl groups which cannot be benzoylated, this substance yields a benzoyl derivative, which melts at 186—187°, is insoluble in alkalis, and dissolves in alcohol with a greenish-yellow fluorescence.

Although flavaspidic acid yields acetyl derivatives when treated with acetic anhydride (compare *loc. cit.*), it does not react with acetic acid or with acetic acid containing hydrogen chloride.

Flavaspidic acid is slowly decomposed by prolonged boiling with alcohol, the *ethyl ether* of dihydroflavaspidylxanthene $\begin{array}{l} CO\cdot CMe_2\text{-}C\text{—}O\text{—}C\cdot C(COPr^{\alpha})\cdot C\cdot OH \\ COPr^{\alpha}\cdot C\colon C(OEt)\cdot C\cdot CH_2\cdot C\cdot C(OH)\text{——}CMe \end{array}$, being formed, and crystallising in red leaflets or prisms melting at 236°. The corresponding *methyl ether*, prepared by boiling the acid with methyl alcohol, crystallises in golden-yellow needles or prisms melting at 249—250°. At the same time, other substances are formed in each case; the *ethyl ether* of dihydroflavaspidic acid, $C_{24}H_{29}O_7(OEt)$, crystallises in pale yellow needles melting at 198—200°, which give a greenish-brown coloration with ferric chloride, and a red coloration and a smell of butyric acid when warmed with sulphuric acid. On digestion with diazoaminobenzene, it is converted into benzeneazomethylphloroglucinyl-*n*-butanone (m. p. 181—182°). The corresponding *methyl* ether crystallises in yellow, rhombic leaflets melting at 201—202°, and yields the same azo-derivative as the ethyl ether when treated with diazoaminobenzene.

Methylphloroglucinyl-n-butanone, $C_6HMe(OH)_3\cdot COPr^{\alpha}$, is also formed in each case, although in greater quantity when ethyl alcohol is used; it crystallises in colourless needles melting at 161—162°, and gives a violet-red coloration with ferric chloride, a brown precipitate afterwards separating.

K. J. P. O.

Aspidin. Rudolf Boehm (*Annalen*, 1903, **329**, 321—337. Compare Abstr., 1898, i, 40; 1899, i, 32, 804; 1902, i, 37).—Aspidin, which has been recently shown (Abstr., 1900, i, 49) never to be present in the extracts of *Aspidium filix mas,* but to be procurable from *Aspidium spinulosum*, is now proved to be identical with "polystichin" (compare Poulsson, Abstr., 1896, i, 387; 1899, i, 379), both the anilide, $C_{31}H_{37}O_7N$, and the compound with phenylhydrazine, $C_{37}H_{42}O_5N_4$, having the same melting points. *Acetylaspidin*, $C_{25}H_{30}O_8Ac_2$, prepared from aspidin by the action of acetic anhydride or acetyl chloride, crystallises in colourless prisms or needles melting at 108°.

Aspidin is more stable towards reagents than other members of the filicic acid group. Under the influence of sodium hydroxide and zinc dust, it is converted into filicic and methylfilicic acids, the β-methyl ether of methylphloroglucinol and butyric acid, but the reaction is not quantitative, as in the case of flavaspidic and filicic acids. A certain proportion of the aspidin always undergoes an intramolecular change, and consequently the calculated amount of butyric acid (2 mols. for each mol. of aspidin) is never obtained.

Whenever aspidin is subjected to the action of hot sodium hydroxide (with or without zinc dust), it is converted into an isomeric substance, ψ-aspidin. This compound crystallises from alcohol or petroleum in pale yellow prisms and has a double melting point; when quickly heated, it melts at 144°, but when slowly heated it either suffers no change at this temperature or only softens, to assume a crystalline habit at a higher temperature; it finally melts at 158—159°. Whilst aspidin contains only one methoxy-group, ψ-aspidin has two; a methyl group must therefore have wandered from a carbon to an oxygen atom. ψ-Aspidin is extremely stable towards alkalis, small quantities of the β-methyl ether of methylphloroglucinol being produced; when treated with sulphuric acid, butyric acid is set free. Towards phenylhydrazine, ψ-aspidin behaves in a similar manner to aspidin, an unstable *compound*, $C_{37}H_{42}O_5N_4$, being formed; it is crystalline and melts at 201—202°. Both aspidin and ψ-aspidin are stable towards diazoaminobenzene, a fact which shows that in neither substance is there a CH group, or a methoxy-group in an ortho-position relatively to a methylene group.

Since among the decomposition products of aspidin the two homologues, filicic and methylfilicic acid, are found, it follows that aspidin is a methylene compound; its molecule consists most probably of the two complexes, filicyl-n-butanone and aspidinol linked together by a methylene group, thus:

$$CO<\begin{matrix}CMe_2\text{———}C(OH)\\C(COPr^a):C(OH)\end{matrix}>C\cdot CH_2\cdot C<\begin{matrix}C(OH)\cdot C(COPr^a)\\C(OMe)\text{===}CMe\end{matrix}>C\cdot OH.$$

The reduction of aspidin affords further evidence for this formula. When treated at 100° with hydriodic acid in the presence of acetic acid, aspidin is converted into two substances; one is identical with dihydroflavaspidylxanthen (preceding page) and melts at 259—260°; aspidin has lost a methoxy-group, and at the same time been converted into an anhydride. The other *product* is the anhydride of aspidin, which has lost one butyryl group; it crystallises in colourless needles melting at 216°, and exhibits a pale bluish-green fluorescence in alcoholic solution; it yields a *monobenzoyl* derivative by the Schotten-Baumann method, crystallising in colourless needles melting at 140—142°, and having an intense blue fluorescence in alcoholic solution.

The facts just mentioned leave little doubt that aspidin is the methyl ether of dihydroflavaspidic acid, and further confirm the suggestion (this vol., i, 406) that in the reduction of flavaspidic acid the four-membered ring is broken.

As regards the constitution of ψ-aspidin, it is probable that the

migration of the methyl group occurs in the filicyl and not in the aspidinol nucleus. K. J. P. O.

Phloraspin. RUDOLF BOEHM (*Annalen*, 1903, **329**, 338—339 Compare Abstr., 1902, i, 37).—During the investigation of large quantities of the pharmacopœal extract of fern, a small amount of a new substance, *phloraspin* (0·15 per cent. of the extract), has been met with. It was obtained in the mother liquors in the preparation of flavaspidic acid and of aspidin. This compound, $C_{23}H_{28}O_8$, crystallises in colourless needles from acetone, melts at 211°, and gives a reddish-brown coloration with ferric chloride; it contains a methoxy-group and behaves towards alkalis and sulphuric acid as do filicic and flavaspidic acids, giving butyric acid. Digestion with alcoholic diazoaminobenzene decomposes phloraspin, benzeneazomethylphloroglucinol *n*-butanone (m. p. 182°) being produced. Hence one-half of the mol. of phloraspin consists of methylphloroglucinol-*n*-butanone, and the other half, which contains the methoxyl group, of the methyl ether of phloroglucinol-*n*-butanone. K. J. P. O.

Derivatives of Asarone. [HERMANN THOMS and] RUDOLF BECKSTROEM (*Arch. Pharm.*, 1904, **242**, 98—104).—Chromyl chloride oxidises dihydroasarone to 4-methoxy-1-propyl-2 : 5-benzoquinone (Abstr., 1903, i, 415, 416), melting at 111°; some asarylaldehyde is formed also.

Dibromoasarone is converted by methyl-alcoholic sodium methoxide in the cold into a *substance*, $C_{13}H_{19}O_4Br$, melting at 77·5°; presumably this is $C_6H_3(OMe)_3{\cdot}CH(OMe){\cdot}CHMeBr$, the α-bromine atom having been replaced by a methoxyl group (compare Auwers and Müller, Abstr., 1902, i, 213). When dibromoasarone is kept for a long time, it becomes transformed into a *substance* with a percentage of bromine corresponding with $C_{24}H_{31}O_6Br$; this melts at 109·5° and is saturated in character.

Asarylaldehyde condenses with acetone in alcoholic solution, in the presence of a little sodium hydroxide, to form the yellow 2 : 4 : 5-*trimethoxybenzylideneacetone*, $C_6H_2(OMe)_3{\cdot}CH{:}CH{\cdot}CMeO$; this melts at 96·5°, its yellow *oxime* at 145°. With methyl nonyl ketone in similar circumstances, 2 : 4 : 5-*trimethoxybenzylidenemethyl nonyl ketone*,

$$C_6H_2(OMe)_3{\cdot}CH{:}CH{\cdot}CO{\cdot}C_9H_{19},$$

is formed; this melts at 97·5°, its yellow *oxime* at 86°, and its yellow *semicarbazone* at 151—152°; it does not form a compound with sodium hydrogen sulphite, and consequently does not contain a ·CMeO group.

Asarylaldehyde, when its alcoholic solution is saturated at 0° with gaseous hydrogen chloride, forms an acetal, 2 : 4 : 5-*trimethoxybenzylidene diethyl ether*, $C_6H_2(OMe)_3{\cdot}CH(OEt)_2$, melting at 101·5°. C. F. B.

Diphenyl-*o*-*m*- and *p*-tolyl-carbinols. SALOMON F. ACREE (*Ber.*, 1904, **37**, 990—994).—*Diphenyl*-p-*tolylcarbinol*, $C_6H_4Me{\cdot}CPh_2{\cdot}OH$, prepared either by the action of sodium phenoxide on phenyl *p*-tolyl ketone, or, better, by the action of magnesium *p*-tolyl bromide on benzophenone, melts at 73—74°, that is, considerably lower than the corresponding ortho-derivative; when oxidised, triphenylcarbinol-*p*-carboxylic

acid is formed. *Diphenyl-o-tolylcarbinol*, prepared in a similar manner from magnesium *o*-tolyl bromide and benzophenone, melts at 98° and boils at 240—245° under 24 mm. pressure. It gives a yellow coloration with sulphuric acid, which vanishes on the addition of water. *Diphenyl-m-tolylcarbinol* melts at 65°, distils at 240—245° under 19 mm. pressure, and gives a reddish-yellow coloration with sulphuric acid. E. F. A.

Arnisterol, the Phytosterol of Arnica Montana. TIMOTHÉE KLOBB (*Compt. rend.*, 1904, 138, 763—765. Compare Abstr., 1903, i, 165).—The author has isolated a new phytosterol (*arnisterol*) from the mixture of hydrocarbons (compare Börner, Diss., Erlangen, 1891) and arnicin, obtained by extracting the flowers of *Arnica montana* with light petroleum. *Arnisterol*, $C_{28}H_{46}O_2$, crystallises from alcohol or alcohol and benzene in well-formed rhombohedral crystals, containing 1 mol. of alcohol of crystallisation, which it loses at 115—120°; it melts at 249—250° (corr.) and sublimes at a higher temperature; is soluble in all the ordinary organic solvents, but crystallises only from alcohol, gives the colour reactions characteristic of phytosterols, and has $[\alpha]_D + 62°8'$. It reacts readily with benzoyl chloride, but no crystalline derivative has been isolated. M. A. W.

Spongosterol, a Cholesterol-like Substance from Suberites Domuncula, and its Probable Relationship to Lipochrome. MARTIN HENZE (*Zeit. physiol. Chem.*, 1904, 41, 108—124).—A cholesterol compound, *spongosterol*, $C_{19}H_{32}O$ (?), has been isolated from the ethereal alcoholic extract of *Suberites domuncula*. It crystallises from 95 per cent. methyl alcohol in glistening plates, melting at 119—120°, and has $[\alpha]_D - 19{\cdot}59°$. It is more readily soluble in alcohol than cholesterol, and also dissolves readily in ether, chloroform, or carbon disulphide, the ethereal solution yielding large, rhomboidal crystals. The crystals give no coloration with 20 per cent. sulphuric acid. The *acetate* melts at 124·5°, the *propionate* at 135—136°, and the *benzoate* at 128°. The *dibromide* (?) crystallises from dilute alcohol in small plates melting at 130°.

The lipochrome which accompanies spongosterol in *Suberites domuncula* has not been obtained in a crystalline form, and does not appear to be transformed, under the influence of light, into spongosterol, but gradually loses its colour owing to oxidation.

The fatty matter contained in the sponge yields, on hydrolysis, an *acid*, $C_{12}H_{24}O_2$ (?), melting at about 110°. J. J. S.

The Nitrile of Hexamethylenecarboxylic Acid. The Amine, $C_6H_{11}{\cdot}CH_2{\cdot}NH_2$, and its Transformation into Suberyl Alcohol. NIKOLAUS J. DEMJANOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 166—176).—*Cyanohexamethylene* (cyclo*hexanecarboxylonitrile*),

$$CH_2<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>CH{\cdot}CN,$$

obtained by converting *cyclo*hexanecarboxylic acid into the chloro-

anhydride, the latter into the corresponding amide by means of aqueous ammonia, and the amide into cyanohexamethylene with phosphoric oxide, is a colourless liquid boiling at 189·5—190° under 755 mm. pressure, and solidifying to a light, crystalline mass melting at 6—7°; it has a sp. gr. 0·9268 at 15°/10°, and 0·9182 at 20°/10°. Reduction with sodium in alcoholic solution yields the *amine*,

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CH_2\cdot NH_2,$$

which is a colourless, viscous liquid boiling at 163° under 740 mm. pressure; it does not solidify at −15°, and its sp. gr. is 0·8896 at 0°/0°, and 0·8738 at 20°/0°; it rapidly absorbs carbon dioxide, giving a slightly soluble salt; its *hydrochloride* forms thick plates melting at about 254°; its *platinichloride* melts at about 240°, and its *picrate* at 184—186°; the *aurichloride* was also prepared. On heating the nitrite of the amine, it decomposes, yielding suberyl alcohol, which was first prepared by reduction of suberone (see Markownikoff, Abstr., 1894, i, 160). This is a case of change from a 6-carbon atom ring to one containing 7 carbon atoms. On oxidation with chromic acid, this alcohol yields suberone, whilst concentrated nitric acid converts it into pimelic acid. T. H. P.

[*cyclo*Hexane Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 148206 and 148207).—Reduction of *cyclo*-Δ^2-hexene-4-one-1-carboxylic acids with sodium and alcohol yields 4-hydroxy*cyclo*hexane-1-carboxylic acids and 4-hydroxy*cyclo*hexane-1-carbinols, together with small quantities of *cyclo*hexenecarboxylic acids.

4-*Hydroxy*-2 : 6-*dimethyl*cyclo*hexane*-1-*carboxylic acid*,

$$\begin{array}{l}\quad CH_2\cdot CHMe\cdot CH\cdot CO_2H\\ OH\cdot CH\cdot CH_2\text{——}CHMe\end{array},$$

from 2 : 6-dimethyl*cyclo*hexene-4-one-1-carboxylic acid, is obtained as an oily mixture of two geometrical isomerides. When distilled under reduced pressure, two *lactones*, $C_9H_{14}O_2$, are obtained, both of which boil at 129—131° under 12 mm. pressure. The γ-lactone is solid, and the δ-lactone liquid. The *ethyl* ester, $OH\cdot C_8H_{14}\cdot CO_2Et$, is obtained from the potassium salt and ethyl iodide, and boils at 144—146° under 16 mm. pressure.

4-*Hydroxy*-2 : 6-*dimethyl*cyclo*hexane*-1-*carbinol*,

$$\begin{array}{l}\quad CH_2\cdot CHMe\cdot CH\cdot CH_2OH\\ OH\cdot CH\cdot CH_2\text{——}CHMe\end{array},$$

is a very viscous oil boiling at 159—161° under 14 mm. pressure, and dissolving readily in water. It is a mixture of two geometrical isomerides. The *diacetyl* derivative, $C_{13}H_{22}O_4$, is an insoluble oil boiling at 160° under 13 mm. pressure.

Ethyl 2 : 6 : 6-Trimethyl*cyclo*-Δ^2-hexene-4-one-1-carboxylate (this vol., i, 317) yields, on reduction, a mixture of hydroxy-acid and carbinol in the proportion 3 : 1. The crude 4-*hydroxy*-2 : 6 : 6-*trimethyl*cyclo*hexane*-1-*carboxylic acid* is a colourless, viscous oil and boils at 176—178° under 8 mm. pressure. The cis-*acid* forms glistening prisms and melts at 141—143°; when heated with potassium hydrogen sulphate, it

forms a *lactone* crystallising in leaflets, melting at 56—57°, and boiling at 122—123° under 9 mm. pressure. The trans-*acid* forms glistening, cubical crystals and melts at 151—153°; heating with potassium hydrogen sulphate converts it into trimethyl*cyclo*hexenecarboxylic acid. The *ethyl* ester, $OH\cdot C_9H_{16}\cdot CO_2Et$, prepared from the mixed acids, is a viscous oil boiling at 150—154° under 17 mm. pressure. It may be oxidised to *ethyl* 2 : 6 : 6-*trimethyl*cyclo*hexane*-4-*one*-1-*carboxylate*, a mobile oil boiling at 132—133° under 12 mm. pressure.

4-*Hydroxy*-2 : 6 : 6-*trimethyl*cyclo*hexane*-1-*carbinol*,

$$\begin{array}{l} \quad\;\; CH_2\cdot CMe_2\cdot CH\cdot CH_2\cdot OH \\ OH\cdot CH\cdot CH_2 \text{—} CHMe \end{array},$$

is a viscous oil boiling at 150—155° under 7—8 mm. pressure, and consists of two isomerides, one of which separates from benzene in colourless crystals, melts at 92—93°, and boils at 152° under 8 mm. pressure.

2 : 6 : 6-Trimethyl*cyclo*-Δ^2-hexene-4-one-1-carboxylic acid, prepared by saponification of the ester, forms crystals and decomposes into *iso*phorone and carbon dioxide on heating. Several methods of reduction are described.

The *cyclo*hexenecarboxylic acids obtained as by-products in the above preparations are best prepared by heating the hydroxy-acids with phosphoric oxide or trichloride, or potassium hydrogen sulphate. 2 : 6-*Dimethyl*cyclo-Δ^4-*hexene*-1-*carboxylic acid* is an oil, solidifying on cooling. The *ethyl* ester is a colourless oil with a fragrant odour, and boils at 89—91° under 12 mm. pressure.

Ethyl 2 : 6 : 6-*trimethyl*cyclo-Δ^4-*hexene*-1-*carboxylate*, prepared by heating ethyl trimethylhydroxy*cyclo*hexanecarboxylate with phosphorus trichloride and quinoline and heating the phosphorous ester first formed under reduced pressure, boils at 95—98° under 13 mm. pressure. The *acid* boils at 140—142° under 15 mm. pressure, and slowly solidifies to colourless crystals on cooling; it is isomeric with α- and β-*cyclo*geranic acids. C. H. D.

Attempts to Synthesise *cyclo*Octane Derivatives. EDUARD BUCHNER AND KURT SCHEDA (*Ber.*, 1904, **37**, 931—938).—*Ethyl* Δ^1-cyclo*heptenecarboxylate*, prepared from the corresponding acid (Braren and Buchner, Abstr., 1900, i, 292; 1901, 85, 385) by heating with alcohol and sulphuric acid, is a colourless oil boiling at 108° under 14 mm. pressure. It reacts with ethyl diazoacetate when heated at 140°, yielding a mixture of esters boiling at 120—175° under 13·5 mm. pressure (the main product distilling at 167°), which is hydrolysed into a mixture of two isomeric acids, $C_{10}H_{14}O_4$. The one crystallises from 100 parts of boiling water in long, colourless needles, melts at 231°, and is not oxidised by permanganate. It contains two carboxylic groups, and forms sparingly soluble *barium*, *calcium*, *lead*, and *silver* salts, but no *anhydride*. The other crystallises from three parts of boiling water in colourless needles, aggregated in clusters, and melts at 132°. It is stable towards permanganate and does not form an anhydride.

Ethyl cyclo*heptanepyrazolinecarboxylate* is obtained as an oil by the interaction of diazomethane and ethyl *cyclo*heptenecarboxylate. It

forms a crystalline *hydrochloride*, $C_8H_{13}N_2{\cdot}CO_2Et,HCl$, which melts and partly decomposes at 150°. It was not found possible to eliminate nitrogen from this compound and so obtain a *cyclo*octane derivative.
E. F. A.

Preparation of Methylenehippuric Acid. CHEMISCHE FABRIK AUF AKTIEN, VORM. E. SCHERING (D.R.-P. 148669).—Aldehydes usually condense with the methylene group of hippuric acid; formaldehyde, however, reacts abnormally.

Methylenehippuric acid, $COPh{\cdot}N{<}\begin{matrix}CH_2{\cdot}CO\\ \quad\;\; | \\ CH_2{\cdot}O\end{matrix}$, prepared by mixing hippuric acid and paraformaldehyde in sulphuric acid solution, or less conveniently by heating the acid with formaldehyde solution and pouring on to ice after 4 days, crystallises from ethyl acetate in large prisms and melts at 151°. It dissolves sparingly in water, more readily in hot benzene or light petroleum. C. H. D.

Soluble, Crystalline Derivatives of Aminocarboxylic Esters. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 147580. Compare following abstract).—The phenolsulphonates of aromatic aminocarboxylic esters are readily decomposed by water, and heating for the purpose of sterilisation is therefore impossible. Stable salts, which may be heated alone or with water to 100° without decomposition, are obtained from acids containing a sulpho-group in the side-chain.

Ethyl p-*aminobenzoate benzylsulphonate*, from ethyl *p*-aminobenzoate hydrochloride and sodium benzylsulphonate, forms white leaflets and decomposes above 235°. *Methyl* m-*amino*-p-*hydroxybenzoate benzylsulphonate* forms long, flat needles and melts and decomposes at 235°. *Methyl* p-*amino*-m-*hydroxybenzoate benzylsulphonate* forms needles and melts and decomposes at 210°. C. H. D.

Compounds of Aromatic Aminocarboxylic Esters with Phenolsulphonic Acids. EDUARD RITSERT (D.R.-P. 147790).—Aromatic aminocarboxylic esters are employed as local anæsthetics, but have the disadvantage of insolubility in water, and their soluble salts with inorganic acids are inapplicable on account of their irritant action. Suitable compounds are obtained from phenolsulphonic acids.

Ethyl p-*aminobenzoate phenol*-o-*sulphonate*,

$$NH_2{\cdot}C_6H_4{\cdot}CO_2Et,OH{\cdot}C_6H_4{\cdot}SO_3H,$$

prepared by mixing warm solutions of sodium phenol-*o*-sulphonate and ethyl-*p*-aminobenzoate hydrochloride, crystallises from alcohol in needles, melts at 201—203°, and is soluble in acetone, insoluble in ether or benzene.

Ethyl p-*aminobenzoate phenol*-p-*sulphonate*,

$$2NH_2{\cdot}C_6H_4{\cdot}CO_2Et,OH{\cdot}C_6H_4{\cdot}SO_3H,$$

forms very large prisms and melts at 158—159°. The normal salt is obtained on boiling with rather more than 1 mol. of free phenol-*p*-sulphonic acid, and crystallises from a mixture of ether and alcohol in tablets melting at 196—198°. *Methyl* p-*aminobenzoate* p-*cresol*-m-*sulphonate* is a normal salt, crystallising in slightly red leaflets; it

melts and decomposes at 216—217°. *Ethyl* p-*aminobenzoate phenol-α-disulphonate* (normal salt) forms slightly yellow, clear crystals, and melts at 220—221°. Water decomposes it partially even in the cold, giving rise to a solution containing about one-third of the total amount of the aminocarboxylate in the free state. C. H. D.

Sulphamic Acids of Aromatic Carboxylic Esters. Hugo Weil (D.R.-P. 147552).—Whilst nitrated aromatic carboxylic acids usually react with sulphites to form sulpho-derivatives of amino-acids, their esters react with alkali hydrogen sulphites to form salts of sulphamic acids of the carboxylic esters, according to the equation: $NO_2{\cdot}Ar{\cdot}CO_2X + 3NaHSO_3 = CO_2X{\cdot}Ar{\cdot}NH{\cdot}SO_3Na + 2NaHSO_4$. If these proportions are used, the sodium hydrogen sulphate produced gives rise to the formation of some amino-carboxylic ester; this may be avoided by the addition of a larger quantity of normal sulphite or hydrogen sulphite. Normal sulphites and acetic acid, or the sulphites of alkali earths, zinc, manganese, &c., or sulphur dioxide and an organic base, may also be employed.

The sodium salts of the sulphamic-carboxylic esters crystallise well from 95 per cent. alcohol. They are not decomposed by cold dilute acids, but heating removes the sulpho-group. Cold sodium hydroxide saponifies the esters.

Sodium methyl o-*sulphamobenzoate*, $CO_2Me{\cdot}C_6H_4{\cdot}NH{\cdot}SO_3Na$, from methyl *o*-nitrobenzoate, crystallises in large groups of needles and melts at 168° (uncorr.); the corresponding *ethyl* ester is a fine crystalline powder and sinters at 90°, melting and decomposing at 110°. *Sodium methyl* m-*sulphamobenzoate* forms rhomboidal crystals and sinters at 121°, melting at 171—172°; the *ethyl* ester forms globular aggregates and melts at 115—116°. *Sodium methyl* p-*sulphamobenzoate* forms slender needles, often twinned, and sinters at 85°, becoming solid on further heating; the *ethyl* ester forms groups of needles, sinters at 55°, then melts and decomposes at 100°, afterwards solidifying. The *ortho*- and *para*-, but not the *meta*-salts, decompose on the water-bath. C. H. D.

[Derivatives of Diphenylamine.] Kalle & Co. (D.R.-P. 148341 and 148342).—*Nitroaminohydroxydiphenylaminecarboxylic acid*, prepared by reducing dinitrohydroxydiphenylaminecarboxylic acid (D.R.-P. 108872), crystallises in small, yellow needles and decomposes on melting; it is insoluble in water, readily soluble in alcohol. The *sodium* salt crystallises in metallic, glistening leaflets. Carbon disulphide converts it into the *thiocarbamidecarboxylic acid*, forming small, yellow crystals, insoluble in water. Fusion with sulphur and alkali sulphide forms a blue dye, insoluble in water, but dissolving in alkali sulphides, and becoming reduced to the leuco-compound on warming.

The *aminothiocarbamide* prepared by the action of carbon disulphide on 2 : 4-diamino-4′-hydroxydiphenylamine is insoluble in water, but dissolves readily in organic solvents, acids or alkalis, and yields a diazo-compound with nitrous acid. C. H. D.

β-Methylcinnamic Acid. GEORG SCHROETER (*Ber.*, 1904, 37, 1090—1093).—*β-Methylcinnamic acid* (*β-phenylcrotonic acid*),
$C_6H_5{\cdot}CMe{:}CH{\cdot}CO_2H$,
prepared by condensing acetophenone with ethyl iodoacetate by means of magnesium and hydrolysing the ester which was formed as an intermediate product and was only partially purified, melts constantly at 97—98·8°, distils completely at 166—168° under 11 mm. pressure, is sparingly soluble in water and in cold carbon disulphide, but readily in alcohol, ether, and chloroform, combines with bromine, decolorises permanganate, and forms insoluble silver, lead, copper, and mercury salts; the silver salt was analysed. T. M. L.

Additive Reactions in Compounds with Conjugated Carbon Linkings. F. WILLY HINRICHSEN (*Ber.*, 1904, 37, 1121—1125. Compare Thiele, Abstr., 1899, i, 554).—Michael and Leighton's results (this vol., i, 242) are confirmed.

[With M. REIMER.]—p-*Nitrophenylcinnamenylacrylic acid*, obtained from sodium *p*-nitrophenylacetate, acetic anhydride, and cinnamaldehyde, crystallises from alcohol in small, yellow needles melting at 259°. The *sodium* salt contains $2H_2O$. When brominated in moist chloroform solution, a *bromo-lactone* melting at 169—171° is obtained. In carbon disulphide solution, a *dibromide*, $C_{17}H_{13}O_4NBr_2$, melting at 207—209°, is formed.

[With W. TRIEPEL.]—*Ethyl cinnamylidenemalonate dibromide* melts at 93°, and on oxidation yields cinnamic acid dibromide, thus indicating the formula $CHPhBr{\cdot}CHBr{\cdot}CH{:}C(CO_2Et)_2$, for the original dibromide. J. J. S.

Pseudonitrosites. A Correction. HEINRICH WIELAND (*Annalen*, 1903, 329, 340).—A question of priority (compare this vol., i, 54, and Angeli, Abstr., 1900, ii, 722; 1902, ii, 254). K. J. P. O.

Action of Formaldehyde on *p*-Nitrophenols. WALTHER BORSCHE and A. D. BERKHOUT (*Annalen*, 1903, 330, 82—107).—In the action of formaldehyde on phenols, the *p*-hydrogen atom is replaced, or if the para-position is already occupied, an *o*-hydrogen atom, in which case a xanthen derivative is often produced. *p*-Nitrophenols behave in a peculiar manner, 2 mols. of the aldehyde reacting with one mol. of the phenol, a methylene ether being formed; thus, from *p*-nitrophenol, the compound $NO_2{\cdot}C_6H_3{<}\begin{matrix}O{-}CH_2\\ CH_2{\cdot}O\end{matrix}$ is obtained (compare Abstr., 1902, i, 836; where this substance was erroneously described as a xanthen derivative). 5-*Nitrosalegeninmethylene ether* is prepared by adding dilute sulphuric acid to a solution of *p*-nitrophenol in 40 per cent. formaldehyde, when much heat is developed, and a mass of crystals separates; the ether crystallises in needles melting at 148° and can be sublimed; by permanganate, it is oxidised to 5-nitrosalicylic acid. When oxidised by chromic acid in acetic acid solution, the *methylene ether ester*, $NO_2{\cdot}C_6H_3{<}\begin{matrix}O{-}CH_2\\ CO{\cdot}O\end{matrix}$, is obtained, crystallising in pale

yellow needles or leaflets melting at 110°, and is converted by alkalis into formaldehyde and 5-nitro-2-hydroxybenzoic acid (m. p. 228°).

5-Nitro-*m*-cresol, prepared by oxidising 5-nitroso-*m*-cresol with potassium ferricyanide, yields a *benzoyl* derivative, crystallises in needles melting at 128°; with formaldehyde, it yields a *methylene ether*, $C_9H_9O_4N$, which crystallises in colourless needles melting at 133°, and is oxidised by chromic acid into the corresponding *ether ester*,

$$NO_2\cdot C_6H_2Me<\begin{matrix}O-CH_2\\ CO\cdot O\end{matrix},$$

crystallising in needles melting at 143°; it is converted by alkalis into nitrocresotic acid (m. p. 199°).

Both 4- and 6-nitro-*m*-cresols are formed in the nitration of *m*-cresol; the *benzoate* of the former forms flattened needles melting at 76°, and the *benzoate* of the latter long, pale yellow needles melting at 75°. Formaldehyde yields with 6-nitro-*m*-cresol a *methylene ether* which crystallises in needles melting at 137°; it is oxidised to the *ether ester*, $NO_2\cdot C_6H_2Me<\begin{matrix}O-CH_2\\ CO\cdot O\end{matrix}$, which forms colourless leaflets melting at 96°. On hydrolysis, it is converted into 6-*nitro*-3-*hydroxy*-2-*cresotic acid*, which crystallises in yellow needles melting at 219°, and was obtained by nitrating 4-methylsalicylic acid.

4-Nitro-α-naphthol and formaldehyde yield two substances which can be separated by taking advantage of the fact that one is soluble in alkalis. The *methylene ether* of 4-nitro-1-hydroxy-2-naphthyl alcohol, $NO_2\cdot C_{10}H_5<\begin{matrix}O-CH_2\\ CH_2\cdot O\end{matrix}$, which is insoluble in alkali, forms brownish-yellow needles melting at 149°; by chromic acid, it is oxidised to the *methylene ether ester*, $NO_2\cdot C_{10}H_5<\begin{matrix}O-CH_2\\ CO\cdot O\end{matrix}$, crystallising in long, pale yellow needles melting at 167—168°; by alkalis, it is hydrolysed, formaldehyde and 4-nitro-1-hydroxy-2-naphthoic acid (m. p. 212°) being formed. The substance, which is soluble in alkali, is 1 : 1′-*dinitro*-4 : 4′-*dihydroxydinaphthylmethane*, which forms lemon-yellow needles melting and decomposing at about 200°. It is oxidised by chromic acid to the corresponding *dinaphthyl ketone*, $CO[C_7H_5(OH)\cdot NO_2]_2$, which is a reddish-brown, amorphous substance, melting and decomposing at 130°.

Formaldehyde and 6-nitroresorcinol (the *dibenzoate* of which crystallises in brownish-yellow needles melting at 109°) yield very small quantities of a *substance*, $C_8H_7O_5N$, which crystallises in needles melting at 130°.
K. J. P. O.

Reduction of Isatin. GUSTAV HELLER (*Ber.*, 1904, 37, 938—950).—Isatyde, $C_{16}H_{12}N_2O_4$, obtained by the reduction of isatin, is shown to be a compound, of the quinhydrone type, of isatin with dioxindol, thus: $C_6H_4<\begin{matrix}CH(OH)-\\ -NH-\end{matrix}>C\begin{matrix}O\cdot O\\ \end{matrix}C<\begin{matrix}CO-\\ NH\end{matrix}>C_6H_4$. *Diacetylisatyde*, formed by reducing acetylisatin, crystallises in small nodules, which sinter at 195° and melt and decompose at 198°; the corresponding *dibenzoylisatyde* melts at 186°. Dioxindole sinters at 160° and melts to a colour-

less mass at 170°; it forms a crystalline *hydrochloride*, which is stable when dry and melts at 156°. *Benzoyldioxindole* crystallises in needles from light petroleum or in prisms from alcohol, and melts at 134°. *Dibenzoyldioxindole*, formed on benzoylating indole in presence of an alkali hydroxide, crystallises from alcohol in needles and melts at 170°. When heated with phenylhydrazine, dioxindole forms isatinephenylhydrazone.

[With KARL AMBERGER.]—The *nitrile* of *o*-nitromandelic acid, prepared by treating *o*-nitrobenzaldehyde with aqueous sodium hydrogen sulphite and adding potassium cyanide to the product, crystallises from benzene in long needles melting at 95°; hydrogen chloride converts this into the *hydrochloride* of o-*nitrophenyloxyacetimidoethyl ether*, which melts and decomposes at 133°.

Ethyl o-*nitromandelate* crystallises in long, colourless needles aggregated in clusters, which melt at 49—50°. When reduced with zinc dust and acetic acid, *o*-nitromandelic acid forms dioxindole, the synthetical substance being in every way identical with that prepared from isatin. E. F. A.

β-Phenyl-β-ethyl-lactic Acid [β-Hydroxy-β-phenylbutyric Acid]. PAUL MICHNOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1188—1192).—*β-Hydroxy-β-phenylbutyric acid*,

$$CH_3 \cdot CH_2 \cdot CPh(OH) \cdot CH_2 \cdot CO_2H,$$

prepared by oxidising phenylethylallylcarbinol by means of potassium permanganate, separates from ether in rhombic plates or prisms which melt at 118—121°, and are readily soluble in water. Its *barium*, *calcium*, and *silver* salts were prepared and analysed. T. H. P.

New Preparation of *o*-Phenoxybenzoic Acid (Salicylic Acid Phenyl Ether). FRITZ ULLMANN (*Ber.*, 1904, **37**, 853—854).—Salicylic acid phenyl ether is conveniently prepared by adding a small quantity of finely-divided copper to a hot solution of potassium *o*-chlorobenzoate in phenol, potassium chloride immediately separating.

[With A. LEHNER.]—*o*-Chlorobenzoic acid and benzenesulphinic acid condense in presence of copper, forming diphenylsulphone-*o*-carboxylic acid. A number of similar condensations are now being studied.

C. H. D.

Preparation of Dialkylphthalides. HUGO BAUER (*Ber.*, 1904, **37**, 735—737).—The methods hitherto in use for preparing dialkylphthalides give very poor yields; that now described, which consists in the action of magnesium alkyl iodides on phthalic anhydride, gives a yield 70—80 per cent. that of theory. In principle, the action is similar to that of magnesium alkyl iodides on acetic and benzoic anhydrides (compare Tissier and Grignard, Abstr., 1901, i, 316), and is indicated as follows:

$$C_6H_4{<}{\substack{CO\\CO}}{>}O + 2MgMeI \longrightarrow C_6H_4{<}{\substack{CMe_2 \cdot OH\\CO_2H}} \longrightarrow C_6H_4{<}{\substack{CMe_2\\-CO-}}{>}O.$$

Dimethylphthalide melts at 67—68°, boils at 274—275° (Kothe gives 271°, Abstr., 1889, 257), and with nitric acid gives a *mononitro*-derivative, which crystallises from light petroleum in slender, felted

needles melting at 131—132°. Diethylphthalide, as stated by Rjasantzeff (Abstr., 1889, 1059), melts at 54° and gives a *nitro*-derivative crystallising in yellow needles and melting at 103—104°.

W. A. D.

Preparation of Nitro-derivatives of Aromatic Amines from Phthalimides. RUDOLF LESSER (D.R.-P. 148874. Compare Abstr. 1903, i, 618).—Nitrophthalamic acids may be combined with aromatic bases in the same way as nitrophthalimides, the reaction taking place at moderate temperatures, so that heating under pressure is not necessary. Phthalimides are recovered, the phthalamic acids formed at first being very unstable. The nitrophthalamic acids may be prepared from phthalimides by conversion into phthalamic acids and subsequent nitration, or by nitration, and conversion into nitrophthalamic acids by boiling with potassium hydroxide. The substances obtained, for example, in the case of the condensation with aniline, are: phthalanil, nitrophthalanil, and nitrophthalamic acid; the last of these, on boiling with aniline, forms nitroaniline and phthalanil. C. H. D.

Transformation of Unsaturated Acids. RUDOLF FITTIG (*Annalen*, 1904, 330, 292—361. Compare Abstr., 1899, i, 332, 417).—In this paper, which is a continuation of the previous work (*loc. cit.*) on the intramolecular changes of unsaturated acids, an account is given of all the possible isomerides of phenyl-paraconic and *iso*paraconic acids (compare Kreutz, Abstr., 1902, i, 462); the four active and the two inactive acids have now been isolated.

Transformation of Methylparaconic into Methylitaconic Acid, and Attempts to obtain Methylaticonic Acid.—[With OSCAR SCHEEN.]—The yield of methylparaconic acid has been improved by directly esterifying the crude acid obtained from ethyl acetosuccinate (Abstr., 1895, i, 204); the *ethyl* ester is a colourless liquid of the consistence of glycerol, boiling at 273—273·5°.

Methylitaconic acid was prepared by the action of sodium ethoxide on ethyl methylparaconate, a yield of 30—35 per cent. of the pure acid (m. p. 166—167°) being obtained. A search was made for by-products by esterifying the oily acids and fractionally distilling the product; *ethyl ethoxyethylsuccinate*, $CO_2Et\cdot CH(CHMe\cdot OEt)\cdot CH_2\cdot CO_2Et$, was obtained as a colourless oil of pleasant smell, boiling at 253—255°; the free *acid* is a colourless, extremely viscid liquid; the *calcium* salt, $C_8H_{12}O_5Ca$, is more soluble in cold than in hot water, the *barium* salt is very soluble, and the *silver* salt is a white powder. When heated with fuming hydrochloric acid under pressure at 140°, this acid is converted into methylparaconic acid.

All attempts to convert methylitaconic into methylaticonic acid by boiling with concentrated sodium hydroxide failed; the major part of the methylitaconic acid was recovered unchanged, a very small amount of methylparaconic acid being alone isolated.

Derivatives of Dimethylaticonic Acid.—[With WALTHER FRIEDMANN.]—(Compare Abstr., 1899, i, 335.) In order to prepare *iso*heptodilactone or hydroxy*iso*terebic acid from dimethylaticonic acid, it is unnecessary to isolate the bromo*iso*terebic acid; the cold aqueous suspension of the

dimethylaticonic acid is treated with the requisite quantity of bromine, saturated with sodium hydroxide, and kept for 24 hours, when an excellent yield of the dilactone is formed; or, in order to prepare the hydroxy*iso*terebic acid, the liquid is diluted after bromination and boiled for ten hours, and then extracted with ether.

Owing to the apparent difficulty of opening the lactone ring of hydroxy*iso*terebic acid on dissolution in an alkali hydroxide (compare *loc. cit.*), it was thought that possibly conversion into the dilactonic acid occurred; this was, however, found not to be the case; only pure hydroxy*iso*terebic acid was recovered from the salts. Similarly, on neutralising the *iso*heptodilactone, both rings are opened, but no transformation takes place, the pure dilactone being obtained from the salts. When, however, hydroxy*iso*terebic acid is neutralised at a higher temperature, a small amount of conversion does occur, the dilactone being obtained from the resulting salt. No transformation of the dilactone takes place in similar circumstances. The *barium* salt, $C_7H_{10}O_6Ba$, derived from the dilactone, is a hygroscopic, crystalline powder, whilst that prepared from hydroxy*iso*terebic acid crystallises with $3\frac{1}{2}H_2O$, $2H_2O$ being lost at 100°. The *barium* salt of the monobasic lactonic acid, $(C_7H_9O_5)_2Ba,2H_2O$, can be prepared from hydroxy*iso*terebic acid, *iso*heptodilactone yielding a similar *barium* salt crystallising with $1H_2O$.

Attempts to convert the dilactone into the hydroxy-acid by the action of concentrated hydrochloric acid, or to convert the hydroxy-acid into the dilactone by heat, failed; it was found, however, that the hydroxy*iso*terebic acid was slowly changed into the dilactone when its solution in excess of sodium hydroxide was kept for 12 days, in this period, 64 per cent. of the dilactone being formed. Under similar conditions, no reverse change of the dilactone into the hydroxy-acid occurs.

Derivatives of Phenylaticonic Acid.—[With ADOLF BRESLAUER.]—Phenylaticonic acid is to a small extent converted into phenylbromo*iso*paraconic acid, $C_5H_4O_4PhBr$, when it is acted on by bromine in chloroform solution in diffused daylight, but it is much more readily produced by carrying out the bromination in the presence of water; the acid crystallises in star-shaped clusters of needles melting at 147°, and belonging to the monoclinic system. Although the melting point of the acid only differs by 3° from that of phenylparaconic acid, which is prepared from phenylitaconic acid (Fittig and Leoni, Abstr., 1897, i, 894), the crystalline habit of the two acids is quite distinct. Both acids yield the same benzoylpropionic acid when boiled with water. On reduction with sodium amalgam, phenylbromo*iso*paraconic acid is converted into a mixture of phenylparaconic acid and phenyl*iso*paraconic acids, the latter being formed in only small quantity; the yield is somewhat increased when the alkalinity is kept as low as possible by addition of sulphuric acid during the reduction. *Phenyl*iso*paraconic acid*, $C_5H_5O_4Ph$, crystallises in leaflets melting at 170° and behaves on neutralisation as a monobasic lactonic acid. The *barium* salt, $(C_{11}H_9O_4)_2Ba$, is a soluble crystalline solid; the *barium* salt, $(C_{11}H_{10}O_5)_2Ba$, of the dibasic hydroxy-acid is crystalline and far less soluble.

Isomeric Phenylparaconic Acids.—[With Paul Jehl.]—Owing to Fichter and Dreyfus' observation (Abstr., 1900, i, 426) that phenylparaconic acid is partly converted into the *iso*paraconic acid by boiling with excess of sodium hydroxide for 24 hours, the conditions of transformation of these acids into each other has been investigated. When phenylparaconic acid is boiled with the alkali hydroxide, 22—25 per cent. of phenylitaconic acid, 30—33 per cent. of phenyl*iso*paraconic acid, and 40—46 per cent. of phenylparaconic acid are produced. When phenyl*iso*paraconic acid is similarly treated, 7 per cent. of phenylitaconic, 31 per cent. of phenyl*iso*paraconic, and 61 per cent. of phenylparaconic acids are obtained. When the *iso*-acid is boiled with water, no change occurs, but when heated under pressure with water, a more complicated decomposition was observed, phenylparaconic and phenyl*iso*crotonic acids, and phenylbutyrolactone being formed. If the *iso*-acid is boiled with dilute hydrochloric acid, it is entirely changed, phenylparaconic and phenyl*iso*crotonic acids, and phenylbutyrolactone being formed. On boiling phenyl*iso*paraconic acid with excess of barium hydroxide, no transformation takes place.

When phenyl*iso*paraconic acid is distilled, it yields the same products as phenylparaconic acid, unchanged acid, phenylbutyrolactone, and phenyl*iso*crotonic acid. This behaviour is due to the fact that phenyl*iso*paraconic acid is largely changed on heating into phenylparaconic acid, which then decomposes into phenyl*iso*crotonic acid.

Phenyl*iso*paraconic acid is decomposed into its two active modifications by the aid of its strychnine salts in the same manner as Kreutz (*loc. cit.*) employed for the phenylparaconic acid. From the insoluble strychnine salt, which crystallises in needles and melts at 120—130°, the *d*-acid was obtained, and from the soluble strychnine salt, which crystallises in plates melting at 165—170°, the *l*-acid. Both acids form large crystals melting at 182°; in alcohol, the *d*-acid has $[\alpha]_D + 14{\cdot}72°$, and the *l*-acid $[\alpha]_D - 14{\cdot}51°$ at 20°; in acetic acid, the *d*-acid has $[\alpha]_D - 6{\cdot}95°$, and the *l*-acid $[\alpha]_D + 7{\cdot}29°$, at 20°. In acetic acid therefore the rotation is reversed. *Penicillium glaucum* also effects a separation of the two forms, destroying the *l*-acid more readily. At a high temperature, each of the acids racemises, but boiling of either acid alone or in the form of its barium salt has no effect. A crystallographic investigation showed that the racemic phenyl*iso*paraconic acid belongs to the monoclinic system [$a:b:c = 2{\cdot}6842:1:2{\cdot}1225$, and $\beta = 80°23'$]; the active acids crystallise in the rhombic system [$a:b:c = 0{\cdot}9022:1:2{\cdot}4024$].

Kreutz's work on phenylparaconic acid has been repeated and in numerous points corrected. The strychnine salts of the active acids are separated by crystallisation from absolute alcohol, the salt of the *l*-acid separating first in plates melting at 197—202°, and the salt of the *d*-acid separating afterwards in needles melting at 100—102°. Each acid crystallises with $\frac{1}{4}H_2O$ from aqueous solvents, but from ether or acetone in forms melting at 134°. The *d*-acid has in alcoholic solution $[\alpha]_D + 64{\cdot}33°$, and the *l*-acid $[\alpha]_D - 65{\cdot}33°$; in acetic acid solution, the *d*-acid has $[\alpha]_D + 75{\cdot}91°$, and the *l*-acid $[\alpha]_D - 76{\cdot}34°$; in all cases, the temperature was 20°. Anhydrous phenylparaconic acid crystallises in monoclinic forms [$a:b:c = 1{\cdot}3644:1:2{\cdot}4853$ and

$\beta = 87°55'$] melting at 121°; the active forms crystallise in the rhombic system [$a:b:c = 1{\cdot}0886:1:x$]. Measurements of the electrical conductivity of the two racemic acids have given the values, for phenylparaconic acid, K 0·000480, and for phenyl*iso*paraconic acid, K 0·000404.

Transformations of Diphenylitaconic Acid.—[With ALFRED RIECHE.]—When boiled with concentrated sodium hydroxide, phenylitaconic acid undergoes no change, but when heated, decomposition occurs. At 170—180° under 20 mm. pressure in a slow current of air, benzophenone distils over, and the residue contains diphenylitaconic anhydride, crystallising in pale yellow needles melting and decomposing at 147—150° (Stobbe and Kohlmann, Abstr., 1899, i, 900). Diphenylcitraconic anhydride, $CHPh_2{\cdot}C{<}\begin{matrix}CH{\cdot}CO\\ \quad\ \ |\\ CO{\cdot}O\end{matrix}$, is formed together with the anhydride last mentioned, and is more soluble in carbon disulphide; it crystallises in colourless prisms and from benzene in plates with 1 mol. of benzene, and melts and decomposes at 96—98°. The acid crystallises in needles melting and decomposing at 105—115° and very readily passes into the anhydride. The *calcium* salt crystallises with $2H_2O$ in needles, the barium salt with $3\frac{1}{2}H_2O$ in prisms, and the silver salt is amorphous. When boiled with 10 per cent. sodium hydroxide or heated with water under pressure at 200°, this acid is completely changed into diphenylitaconic acid. Treatment of the diphenylcitraconic acid with bromine in sunlight did not lead to the formation of diphenylmesaconic acid; the use of dilute nitric acid was equally fruitless. On reduction with sodium amalgam, this acid is converted into diphenylmethylsuccinic acid. K. J. P. O.

Hexahydro-*m*-tolualdehyde. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1904, **37**, 850—853. Compare Bouveault, this vol., i, 61).—*m*-Bromomethyl*cyclo*hexane, prepared by reducing an ethereal solution of *m*-methyl*cyclo*hexanone with sodium, saturating with hydrogen bromide, and warming, is optically inactive. It reacts vigorously with magnesium powder, and the product reacts with ethyl orthoformate to form the acetal, which is distilled, the fraction boiling above 120° being hydrolysed by means of 5 per cent. hydrochloric acid. The aldehyde is isolated by decomposing its sodium hydrogen sulphite compound with sodium carbonate. *Hexahydro*-m-*tolualdehyde*, $C_6H_{10}Me{\cdot}CHO$, boils at 176—178° under 760 mm., and at 96—97° under 50 mm. pressure, a small quantity of a less volatile aldehyde being formed after a time or on heating. It has a sharp, naphtha-like odour, and has a sp. gr. 0·9279 at 0/0°, and 0·9091 at 20°/0°. The *semicarbazone* crystallises from a mixture of alcohol and light petroleum in needles and melts at 158—159°, insoluble in water, very soluble in alcohol, acetone, or chloroform, sparingly so in benzene.

In addition to the acetal, small quantities of methyl*cyclo*hexene and dimethyldi*cyclo*hexyl are obtained. C. H. D.

A General Method of Synthesising Aldehydes. F. BODROUX (*Compt. rend.*, 1904, **138**, 700—701).—It has already been shown (this vol., i, 250) that ethyl orthoformate reacts with aromatic organo-

magnesium compounds giving the ethylacetal of an aromatic aldehyde. The yield of the latter is never very good, and diminishes with increase of carbon in the aromatic radicle. It is found that better yields are obtained by operating at higher temperatures. Dry toluene (150 grams for every gram-atom of magnesium) is added to the ethereal solution of the organo-magnesium compound and the excess of ether distilled off. The residue is maintained at 100° and the orthoformate ($\frac{2}{3}$—$\frac{3}{4}$ mol.) gradually added ; after the reaction is over, the acetal can be isolated in the usual manner. The following aldehydes were prepared : phenylacetaldehyde, *a*-naphthaldehyde, *p*-bromobenzaldehyde, *p*-chlorobenzaldehyde, butaldehyde, and *iso*valeraldehyde. The yields varied from 55 per cent. in the case of phenylacetaldehyde to 75 per cent. in butaldehyde. S. S.

Action of Methyl Sulphate on Anthranil and *o*-Aminobenzaldehyde. EUGEN BAMBERGER (*Ber.*, 1904, 37, 966—990. Compare Heller, this vol., i, 160).—It is shown that the supposed N-methylanthranil, $C_6H_4<{NMe \atop CO}>$, described by Heller, which differed very considerably in its properties from Bamberger's *C*-methylanthranil, $C_6H_4<{N \atop \overset{||}{C}Me}>O$, as also from anthranil itself, is, in reality, a mixture of *o*-dimethylaminobenzaldehyde, *o*-methylaminobenzaldehyde, and a small quantity of *o*-aminobenzaldehyde. *o-Dimethylaminobenzaldehyde*, $NMe_2 \cdot C_6H_4 \cdot CHO$, which is formed in quantity by the action of methyl sulphate on anthranil in the cold, is a light yellow oil boiling at 120° under 11 mm. pressure. The following derivatives have been characterised : the golden-yellow, crystalline *mercurichloride* melts between 90° and 95° to a syrup, and on further heating becomes brown at 135° ; the *platinichloride* forms needles, which melt and decompose at 205—206° ; the *aurichloride* softens at 121° and melts at 124—125° ; the *stannichloride* crystallises in colourless needles or glistening prisms from hydrochloric acid, which melt and decompose at 226—230°. The *sulphite* forms colourless, glistening needles or prisms and melts and decomposes at 162° ; the *p-nitrophenylhydrazone* crystallises from alcohol in compact, glistening, reddish-purple prisms with a metallic lustre, melts at 190·5—191°, and forms a *hydrochloride*, which crystallises in orange-yellow, silky, glistening needles. The *phenylhydrazone* crystallises from dilute hydrochloric acid in straw-yellow needles melting at 74—74·5°. *o-Dimethylaminobenzaldoxime*, $NMe_2 \cdot C_6H_4CH \colon N \cdot OH$, forms colourless, silky, glistening needles melting at 87—87·2°. *o-Aldehydophenyltrimethylammonium iodide*, $(CHO \cdot C_6H_4 \cdot NMe_3)I$, prepared by combining the aldehyde with methyl iodide, crystallises from alcohol in colourless, nacreous, glistening plates resembling naphthalene, which melt and decompose at 163·5°.

o-Methylaminobenzaldehyde, $NHMe \cdot C_6H_4 \cdot CHO$, is also formed when methyl sulphate acts on anthranil, and is obtained in quantity by slightly modifying the conditions. The following derivatives have been prepared to characterise it : the *mercurichloride* forms golden-yellow, glistening needles, which soften at 105° and melt to a black liquid at 141—142° ; the yellow needles of the *platinichloride* melt at

200—201°; the *aurichloride* is obtained as a light yellow, crystalline product, which rapidly darkens; the *stannichloride* forms colourless, glistening prisms, which melt at 208—209°. *Benzoylmethylaminobenzaldehyde*, $NMeBz\cdot C_6H_4\cdot CHO$, crystallises in white, glistening needles melting at 78·5—79°; the *phenylhydrazone* forms pale yellow, almost colourless, silky needles melting at 124·5—125·5°; the *p-nitrophenylhydrazone* crystallises in deep bordeaux-red, glistening needles with a greenish-gold lustre, and melts at 245—246°.

The *oxime* forms snow-white, silky needles melting at 50·5—51°; *anhydromethylaminobenzaldehyde*, $C_{16}H_{16}ON_2$, crystallises from light petroleum in strongly refractive, colourless, glistening prisms melting at 139·5—140°.

The *o*-mono- and *o*-di-methylaminobenzaldehydes prepared directly by methylation of aminobenzaldehyde with methyl sulphate were in every way identical with the compounds formed from anthranil.

E. F. A.

Preparation of *p*-Alkylaminobenzaldehydes. FRITZ ULLMANN and BURKHARD FREY (*Ber.*, 1904, 37, 855—866).—Alkylated anilines combine with formaldehyde in presence of hydrochloric acid to form alkylaminobenzyl alcohols. Nitrosodimethylaniline oxidises these to the corresponding aldehydes, together with the anhydro-base. This method may be used for the preparation of alkylaminobenzaldehydes.

Ethylaniline, formaldehyde, *p*-nitrosodimethylaniline, and hydrochloric acid react together on warming. The product is best converted, by addition of sulphanilic acid, into p-*ethylaminobenzylidenesulphanilic acid*, which forms a reddish-brown, insoluble, crystalline powder. Alkalis decompose it, forming p-*ethylaminobenzaldehyde*, which crystallises in colourless needles, melts at 79°, dissolves readily in alcohol, ether, benzene, hot water, or boiling light petroleum. The *phenylhydrazone* forms yellow needles, dissolving readily in benzene or glacial acetic acid, sparingly in hot alcohol, and melts at 178°; the *oxime* melts at 118° and dissolves readily in alcohol, benzene, or sodium hydroxide.

p-Dimethylaminobenzaldehyde (Bössneck, Abstr., 1886, 874) may be prepared from *p*-dimethylaminobenzylideneaminodimethylaniline (Möhlau and Fritzsche, Abstr., 1893, i, 470) by the action of either nitrous acid or formaldehyde. The *phenylhydrazone* crystallises in yellow needles and melts at 148°.

p-*Diethylaminobenzylidenephenylhydrazone* forms large, yellowish-brown needles and melts at 103°; the *oxime* melts at 93°.

The condensation-product from methylethylaniline is p-*methylethylaminobenzylidene*-p-*aminodimethylaniline*, crystallising from benzene in slender, yellow needles and melting at 216°, dissolving readily in benzene, sparingly in hot alcohol. Boiling with formaldehyde and acetic acid forms p-*methylethylaminobenzaldehyde*, which melts at 14° and boils at 180° under 20 mm. pressure. The *phenylhydrazone* forms brownish-yellow needles and melts at 114°.

Methyl-*o*-toluidine, formaldehyde, hydrochloric acid, and nitrosodimethylaniline form p-*methylamino*-m-*methylbenzylidene*-p-*dimethyl-*

aminoaniline, $NHMe\cdot C_6H_3Me\cdot CH{:}N\cdot C_6H_4\cdot NMe_2$, which crystallises from alcohol in small, yellowish-green prisms, melts at 162°, and dissolves readily in benzene or hot alcohol. Acetic acid and formaldehyde decompose it, forming 6-*methylamino-3-tolualdehyde*, which forms slender, almost colourless, glistening needles, melts at 115°, and crystallises from boiling water in leaflets. The *phenylhydrazone* forms yellow needles and melts at 124°. 6-*Ethylamino-3-tolualdehyde*, prepared in similar manner, crystallises in slightly yellow, glistening prisms and melts at 69·5°. The *phenylhydrazone* forms yellow needles and melts at 95°; the *oxime* forms colourless leaflets and melts at 82°.

2-*Chloro-4-dimethylaminobenzaldehyde*, from *m*-chlorodimethylaniline, crystallises from light petroleum in almost colourless needles and melts at 82°; the *phenylhydrazone* forms yellow needles and melts at 122°. Nitric and sulphuric acids form 2-*chloro-5-nitro-4-dimethylaminobenzaldehyde*, which forms large, yellow prisms and melts at 125°; the *phenylhydrazone* crystallises in reddish-violet needles, melts at 166°, and dissolves in hot benzene or acetic acid to orange solutions. The *oxime* forms orange needles and melts at 178°. *Chloronitrodimethylaminobenzylideneaniline* crystallises in brick-red needles and melts at 118°. The aldehyde also condenses with benzenesulphinic acid, forming 4-*nitrodimethylaminodiphenylsulphone-2-aldehyde* (compare Abstr., 1901, i, 383), which forms yellow leaflets melting at 96°. C. H. D.

Nitro-*p*-dimethylaminobenzaldehyde. Emilio Noelting and Jules Demant (*Ber.*, 1904, 37, 1028—1032).—On oxidising 3-nitro-4-dimethylaminobenzaldehyde with alkaline potassium permanganate, 3-*nitro-4-methylaminobenzoic acid*, $NHMe\cdot C_6H_3(NO_2)\cdot CO_2H$, is obtained, not the corresponding dimethylaminobenzoic acid; it crystallises from alcohol in yellow needles, melts at 288°, and on acetylation gives the *acetyl* derivative, $NMeAc\cdot C_6H_3(NO_2)\cdot CO_2H$, which forms yellow needles and melts at 190°; the *ethyl* ester, $NHMe\cdot C_6H_3(NO_2)\cdot CO_2Et$, crystallises from alcohol and melts at 101—102°.

3-*Nitro-4-dimethylaminobenzaldoxime*, prepared from the aldehyde and hydroxylamine, crystallises from alcohol in large, orange-coloured prisms melting at 132° and, when heated with acetic anhydride and sodium acetate, is converted into 3-*nitro-4-dimethylaminobenzonitrile*, which forms four-sided, yellow leaflets and melts at 114—115°. 3-*Nitro-4-dimethylaminobenzoic acid*, obtained by hydrolysing the nitrile with alcoholic sodium hydroxide, forms bright yellow needles, melts at 214—215°, and gives an *ethyl* ester, crystallising in leaflets, and melting at 80—81°; the same acid is obtained by directly nitrating *p*-dimethylaminobenzoic acid. On oxidising 3-nitro-4-dimethylaminobenzoic acid with alkaline potassium permanganate, the foregoing 3-nitro-4-methylaminobenzoic acid is formed. W. A. D.

Terpenes and Ethereal Oils. Transformation of 1 : 3- into 1 : 2-Methyl*cyclo*hexanone. Otto Wallach [with Ulrich Franke] (*Annalen*, 1903, 329, 368—380).—In order to study further the transformation of one cyclic hexanone into an isomeride (Abstr., 1902, i, 806), the transformation of 1-methyl-3-*cyclo*hexanone into 1-methyl-

2-*cyclo*hexanone has been effected. 1-Methyl*cyclo*hexanone was obtained from a tetrahydrotoluene, an account of which has previously been given (Abstr., 1902, i, 750). The *nitrosate* of tetrahydrotoluene crystallises in needles melting at 107—108°. When the hydrocarbon is oxidised at 0° by one per cent. permanganate, δ-acetylvaleric acid is obtained, and can be isolated as the semicarbazone (m. p. 144—146°); the hydrocarbon must therefore be represented by the formula $CH_2<\begin{matrix}CH_2-CH\\CH_2\cdot CH_2\end{matrix}>CMe$, and is probably identical with the hydrocarbon (b. p. 108°) obtained by Markownikoff (Abstr., 1900, i, 579) and called "α-naphthylene."

When the nitrosate is warmed with sodium methoxide, an *oxime* is obtained, which forms crystals melting at 40—42°, and boils at 115—117° under 11 mm. pressure (compare *loc. cit.*). It yields two benzoyl derivatives, an *α-compound*, which crystallises in needles melting at 142—143°, and is sparingly soluble in ether, and a *β-compound* melting at 90—91° and readily soluble in ether. On boiling the oxime with hydroxylamine hydrochloride, it undergoes an isomeric change into an *oxime* which melts at 62—63°, and yields a *benzoyl* derivative melting at 142—143°. By warming with sulphuric acid, both oximes are converted into methyl*cyclo*hexenone, the sp. gr. of which is now given as 0·9680, and the n_D as 1·4831 at 20° (compare *loc. cit.*). The *semicarbazone* melts at 207—208°.

1 : 2-*Methyl*cyclo*hexanol*, $C_7H_{13}\cdot OH$, prepared by reducing the methyl*cyclo*hexenone by sodium and alcohol (Abstr., 1902, i, 801), boils at 168—170° and has a sp. gr. 0·921 and n_D 1·4696; the *phenylurethane* obtained from it melts at 103—104°.

The methyl*cyclo*hexanol is oxidised by chromic acid to 1 : 2-methyl*cyclo*hexanone, which was found to be identical with the compound synthesised from methyladipic acid by Zelinsky and Generosoff (Abstr., 1896, i, 350); it has n_D 1·4461 at 21·5°, and forms an *oxime* melting at 43—44°, the *benzoyl* derivative of which melts at 70—72°. When oxidised by chromic acid in the presence of dilute sulphuric acid, δ-acetylvaleric acid is formed; its constitution was fixed by oxidising it to adipic acid by means of sodium hypobromite. K. J. P. O.

Preparation of ψ-Ionone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 147839).—In the preparation of ψ-ionone by the condensation of citral with acetone, the yield is considerably improved when the reaction is carried out in the absence of water. Sodamide or potassamide is employed as a condensing agent, and benzene is added, if necessary, to dilute the reacting substances. C. H. D.

Action of Phosphorus Pentasulphide on Benzophenoneoxime. R. CIUSA (*Gazzetta*, 1904, 34, i, 102—104).—Phosphorus pentasulphide reacts explosively with benzophenoneoxime at 80°; in boiling carbon disulphide solution, the action takes place smoothly, a *substance*, $C_{10}H_{10}O_3S$, being formed, which crystallises from aqueous alcohol in plates, melts at 86°, and, on reduction with zinc and hydrochloric acid, evolves hydrogen sulphide. W. A. D.

Conversion of Dibenzylideneacetone into Derivatives of Diphenyl*cyclo*pentane. DANIEL VORLÄNDER and HEINRICH VON LIEBIG (*Ber.*, 1904, 37, 1133—1134).—The compound, $C_{17}H_{14}O_2$, obtained by Vorländer and Schrödter (Abstr., 1903, i, 496) by the action of acetic anhydride and sulphuric acid on dibenzylideneacetone may be regarded as a derivative of *cyclo*pentane, the β-carbon atoms having become linked together. This view is confirmed by the oxidation of the compound to benzil and desylacetic acid by chromic acid or potassium permanganate. It is therefore a keto-enolic compound having the formula $\begin{matrix}CHPh-CH_2\\ | \\ CPh:C(OH)\end{matrix}\!\!>\!CO$, and is isomeric with anhydroacetonebenzil, $\begin{matrix}OH\cdot CPh\cdot CH_2\\ | \\ CPh{=}CH\end{matrix}\!\!>\!CO$ (Japp, Burton, and Lander, Trans., 1887, 51, 420; Proc., 1896, 108), which has no acid properties. Hydriodic acid reduces both compounds to the same diphenyl*cyclo*pentane,

$$\begin{matrix}CHPh\cdot CH_2\\ | \\ CHPh\cdot CH_2\end{matrix}\!\!>\!CH_2.$$

The hydrocarbon, $C_{15}H_{14}$, obtained by the action of concentrated potassium hydroxide on the keto-enolic compound and described as an α-methylstilbene, is identical with the α-methylstilbene prepared by Klages (Abstr., 1902, i, 668) from deoxybenzoin and magnesium methyl iodide, and by Hell (this vol., i, 242) from acetophenone and magnesium benzyl chloride, although the melting points of the hydrocarbon and its dibromide show slight differences. C. H. D.

Synthesis of Yellow Vegetable Dyes. STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1904, 37, 792—794).—*2'-Hydroxy-4' : 6' : 4-trimethoxychalkone*,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH:CH\cdot C_6H_4\cdot OMe,$$

prepared from phloracetophenone dimethyl ether and anisaldehyde, crystallises from alcohol in yellow needles and melts at 113°. The *acetyl* derivative, $C_{20}H_{20}O_6$, crystallises from alcohol in pale yellow flakes and melts at 120°.

2'-Hydroxy-4' : 6' : 3 : 4-tetramethoxychalkone,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH:CH\cdot C_6H_3(OMe)_2,$$

prepared from phloracetophenone dimethyl ether and veratraldehyde, crystallises from alcohol in yellow flakes and melts at 157°. The *acetyl* derivative, $C_{21}H_{20}O_7$, crystallises from dilute alcohol in pale yellow needles and melts at 107°.

2'-Hydroxy-4' : 6' : 2 : 4-tetramethoxychalkone,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH:CH\cdot C_6H_3(OMe)_2,$$

prepared from phloracetophenone dimethyl ether and 2 : 4-dimethoxybenzaldehyde, crystallises from a mixture of benzene and light petroleum or from alcohol in deep yellow needles and melts at 152°. The *acetyl* derivative, $C_{21}H_{20}O_7$, crystallises from alcohol in bright yellow needles and melts at 118—119°.

It is proposed, by applying the methods described later (this vol., i, 440, 441), to synthesise from this series of *o*-hydroxychalkones the natural dyes galangin, kaempferol, quercetin, and morin. T. M. L.

Reactions of Unsaturated Ketones. CARL D. HARRIES (*Annalen*, 1904, 330, 185—279).—In the long introduction to this paper, a very detailed account is given of our present knowledge of the properties of unsaturated ketones; the nature of the ethylene linking is also discussed, and two or three instances of addition to a conjugated pair of ethylene linkings are quoted, which are not in agreement with Thiele's hypothesis of partial valence.

I. *Aromatic aβ-Unsaturated Ketones.*—[With FRIEDRICH GOLLNITZ.]—*Dypnonehydroxylamine*, CMePh(NH·OH)·CH_2·COPh, is formed whenever dypnone and hydroxylamine are kept together in alcoholic solution for several days; it forms a colourless, crystalline substance melting at 109—110°, reduces Fehling's solution, and is oxidised to an unstable, blue nitroso compound; its *acid oxalate*, $C_{18}H_{19}O_6N$, melts at 63°; with phenylcarbimide, it yields a *carbamide*, $C_{23}H_{22}O_3N_2$, which is a microcrystalline powder melting at 127°, and with phenylhydrazine a *phenylhydrazone*, $C_{22}H_{23}ON_3$, which is a microcrystalline substance melting at 125—126°. In the formation of dypnonehydroxylamine, a by-product is obtained which appears to be *diphenylpyrazine*, melting at 193°.

On reducing dypnone with sodium amalgam in alcoholic solution, 1-*benzoyl-2-phenylpropane*, CHMePh·CH_2·COPh, is obtained as crystals melting at 72° and boiling at 200° under 18 mm. pressure; its *phenylhydrazone* melts at 78—79°.

Benzylbenzylideneacetone, CHPh:CH·CO·CH_2·CH_2Ph, prepared by condensing benzylacetone with benzaldehyde in the presence of sodium hydroxide, crystallises in yellow leaflets melting at 53°; its *phenylhydrazone* crystallises in yellow needles melting at 116°; the *oxime* forms small, colourless crystals melting at 95—105°. On reduction, benzylbenzylideneacetone is reduced to dibenzylacetone and to a *diketone*, $C_2H_2Ph_2(CH_2\cdot CO\cdot CH_2\cdot CH_2Ph)_2$, which remains behind on distilling the mixture, and forms crystals melting at 171—172°.

Benzylacetylacetone, CHPh·CHAc·COMe, prepared by reducing benzylideneacetylacetone by sodium amalgam, is a colourless oil, boiling at 151—152° under 16 mm. pressure, and has a sp. gr. 1·063 at 15°. On reducing methoxybenzylideneacetone, two substances are obtained, *methoxybenzylacetone*, OMe·C_6H_4·CH_2·CH_2·COMe, which is an oil boiling at 160° under 22 mm. pressure and has a sp. gr. 1·0504 at 22°; it forms a *phenylhydrazone* melting at 107—108°; the other substance, *δε-dianisylocta-βη-dione*, $C_2H_2(C_6H_4\cdot OMe)_2(CH_2\cdot COMe)_2$, crystallises in needles melting at 151—152°, and yields a *phenylhydrazone*, crystallising in colourless needles melting at 180°.

II. *Action of Nitrous and Nitric Acids on aβ-Unsaturated Aromatic Oximino-compounds.*—[With HEINRICH TIETZ].—*Oximinobenzoylmethylglyoxime peroxide*, $OH\cdot N{:}CPh\cdot CH_2\cdot C{\lessdot}\begin{matrix}CH{:}N\\ N{-}{-}O\end{matrix}{>}O$ (compare Abstr., 1900, i, 504), is prepared by adding an aqueous solution of sodium nitrite to benzylideneacetoxime in acetic acid, and crystallises in red leaflets melting at 215°; the *sodium* derivative forms lustrous, green crystals, and reduces Fehling's solution; the *acetyl* derivative, prepared by the action of acetic anhydride on the peroxide, crystallises in reddish-yellow needles melting at 150—154°. When oxidised with perman-

ganate, or heated with hydrochloric or nitric acids, benzoic acid is alone formed. When oxidised by concentrated nitric acid, p-*nitrobenzoylmethylglyoxime peroxide*, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}C}\leqslant\substack{\mathrm{CH:N}\\ \mathrm{N{-}{-}O}}>\mathrm{O}$, is formed in small quantity, crystallising in yellow needles melting at 197—198°; on hydrolysis with hydrochloric acid, *p*-nitrobenzoic acid is alone produced. When benzylideneacetoxime is kept in contact with nitric acid for a long time in the cold, *benzoylmethylglyoxime peroxide*, $\mathrm{CH_2Bz{\cdot}C}\leqslant\substack{\mathrm{CH:N}\\ \mathrm{N{-}{-}O}}>\mathrm{O}$, is produced; it crystallises in reddish-yellow crystals melting at 158—159°.

p-Methoxybenzylideneacetoxime, which crystallises in needles melting at 119—120°, is converted by the action of nitrous acid into *oximinoanisoylmethylglyoxime peroxide*,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}C(N{\cdot}OH){\cdot}CH_2{\cdot}C}\leqslant\substack{\mathrm{CH:N}\\ \mathrm{N{-}{-}O}}>\mathrm{O},$$

which crystallises in small, red leaflets melting at 197—198°; its *acetyl* derivative forms brick-red needles melting at 168—169°.

p-*Methoxybenzoylmethylglyoxime peroxide*,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}C}\leqslant\substack{\mathrm{CH:N}\\ \mathrm{N{-}{-}O}}>\mathrm{O},$$

prepared from the corresponding acetoxime and dilute nitric acid, crystallises in brick-red crystals melting at 159—160°.

Oximinocuminoylmethylglyoxime peroxide,

$$\mathrm{C_6H_4Pr^\beta{\cdot}C(N{\cdot}OH){\cdot}CH_2{\cdot}C}\leqslant\substack{\mathrm{CH:N}\\ \mathrm{N{-}{-}O}}>\mathrm{O},$$

is prepared from cuminylideneacetoxime, and crystallises in red needles melting at 187°; when oxidised with nitric acid, a *compound* is formed which melts at 87—88°.

Oximinobenzoyldimethylglyoxime peroxide,

$$\mathrm{OH{\cdot}N{:}CPh{\cdot}CH_2{\cdot}C}\leqslant\substack{\mathrm{CH:N}\\ \mathrm{N{-}{-}O}}>\mathrm{O},$$

prepared from α-benzylidene-ethylmethylketoxime, crystallises in red leaflets melting at 195°; its *acetyl* derivative crystallises in orange-yellow needles melting at 146—147°. γ-Benzylidene-ethylmethylketoxime, when similarly treated, yields a colourless substance, melting at 154—155°, which appears to be the *nitrimine*,

$$\mathrm{CHPh{:}CMe{\cdot}CMe{:}N{\cdot}NO_2}.$$

III. *Action of Oxides of Nitrogen on Oximino-compounds.*—[With W. SLOAN MILLS.] (Compare Abstr., 1902, i, 184, and preceding section).—*Benzylideneisonitrosoacetoxime*, $\mathrm{CHPh{:}CH{\cdot}C({:}N{\cdot}OH){\cdot}CH{:}N{\cdot}OH}$, prepared from benzylidene*iso*nitrosoacetone (obtained from benzaldehyde and *iso*nitrosoacetone) and hydroxylamine, crystallises in long, colourless prisms melting and decomposing at 201—202°. Attempts to oxidise the acetoxime with nitrous acid were fruitless, but on passing nitrous fumes into the ethereal solution *benzylidenemethylglyoxime peroxide nitrosate*, $\mathrm{NO_2{\cdot}CHPh{\cdot}CH_2{\cdot}C}\leqslant\substack{\mathrm{CH:N}\\ \mathrm{N{-}{-}O}}>\mathrm{O}$, was obtained as white, unstable needles melting at 101—102°. When heated in benzene, nitrous fumes are evolved, and *benzylidenemethylglyoxalketoxime*, $\mathrm{CHPh{:}CH{\cdot}C(N{\cdot}OH){\cdot}CHO}$, is formed; it crystallises in brown needles

melting at 103—104°, the alkaline solution of which reduces Fehling's solution in the cold; it forms two *semicarbazones*, which can be separated by taking advantage of their different solubility in acetic acid; the soluble *semicarbazone* crystallises in long needles melting and decomposing at 225—226°, and the insoluble *semicarbazone* melts at 242°.

m-*Nitrobenzylidene*iso*nitrosoacetone*,

$$NO_2\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot CH\colon N\cdot OH,$$

is prepared by treatment of a mixture of *m*-nitrobenzaldehyde and *iso*nitrosoacetone with warm sodium hydroxide, and forms pale yellow needles melting and decomposing at 164°; the *phenylhydrazone* crystallises in yellow needles melting at 99—100°; when heated with phenylhydrazine (2 mols.), the hydroxylamine is eliminated and a diphenylhydrazone melting at 206—207° is formed. The *oxime* is a white, crystalline powder melting at 220°, and the *semicarbazone* a powder melting and decomposing at 196—197°.

*Cuminylidene*iso*nitrosoacetone*, $C_6H_4Pr^{\beta}\cdot CH\colon CH\cdot CO\cdot CH\colon N\cdot OH$, prepared from cuminaldehyde and *iso*nitrosoacetone, crystallises in sulphur-yellow plates, melting at 162—163°; its *semicarbazone* is a white powder melting and decomposing at 176°, and the *oxime* crystallises in needles melting and decomposing at 192°. Although nitrous fumes convert benzylideneacetoxime into benzoylmethylglyoxime peroxide, benzylidene*iso*nitrosoacetone yields, when treated in ethereal solution with this reagent, the *pseudo-nitrole*,

$$CHPh\colon CH\cdot CO\cdot CH(NO)\cdot NO_2,$$

which crystallises in yellow plates melting at 123—124°, reduces Fehling's solution, and gives Liebermann's nitroso-reaction.

IV. *α- and γ-Cuminylidenebutanone and its Transformation Products.* —[With THEODOR ST. WARUNIS.]—*α-Cuminylidenebutanone*,

$$C_6H_4Pr^{\beta}\cdot CH\colon CH\cdot COEt,$$

is prepared by shaking cuminaldehyde and methyl ethyl ketone with 33 per cent. sodium hydroxide for ten days and fractionating the oil under reduced pressure, when the ketone boils at 170° under 17 mm. pressure; it crystallises in leaflets melting at 32—33°, has a sp. gr. 0·9875, and n_D 1·56583 at 20°. The *phenylhydrazone* crystallises in needles melting at 87·5°, and the *semicarbazone* in small needles melting at 193° (corr.). The *oxime* could not be isolated in the pure state, but was immediately converted by treatment with sodium nitrite and acetic acid into the *glyoxime peroxide*,

$$C_6H_4Pr^{\beta}\cdot C(N\cdot OH)\cdot CH_2\cdot C{<}{\begin{matrix}CMe\colon N\\ N\text{——}O\end{matrix}}{>}O,$$

which forms large crystals melting and decomposing at 166°. *Dibromo-α-cuminylidenebutanone*, $C_{14}H_{18}OBr_2$, prepared from the ketone and bromine in acetic acid solution, crystallises in colourless needles melting at 141° (corr.).

On reduction, α-cuminylidenebutanone is converted into *α-cuminylbutanone*, $C_6H_4Pr^{\beta}\cdot CH_2\cdot CH_2\cdot COEt$, which is an oil boiling at 160—164° under 17 mm. pressure, and has a sp. gr. 0·9582 and n_D 1·51321 at 20°, and *εζ-dicumenylocta-εθ-dione*,

$$C_2H_2(C_6H_4Pr^{\beta})_2(CH_2\cdot COEt)_2,$$

which remains after the distillation of the butanone, and crystallises in white needles melting at 169·5° (corr.).

When cuminaldehyde and methyl ethyl ketone are condensed in the presence of hydrochloric acid, γ-*cuminylidenebutanone*,

$$C_6H_4Pr^{\beta}\cdot CH{:}CMe\cdot COMe,$$

is obtained as an oil boiling at 171·5° (corr.) under 17 mm. pressure and having a sp. gr. 0·9858 and n_D 1·56512 at 22°; the *semicarbazone* crystallises in rhombic leaflets melting at 177·5° (corr.), and the *phenylhydrazone* in white needles melting at 106·5° (corr.), and the *oxime* in large, monoclinic prisms melting at 116·5° (corr.). Under the influence of nitrous acid, the oxime is converted into a *nitroimine*,

$$C_6H_4Pr^{\beta}\cdot CH{:}CMe\cdot CMe{:}N\cdot NO_2,$$

crystallising in rhombic plates, melting and decomposing at 169·5° (corr.). *Dibromo-γ-cuminylidenebutanone* was only obtained as an oil. On reduction, γ-cuminylidenebutanone yields γ-*cuminylbutanone*,

$$C_6H_4Pr^{\beta}\cdot CH_2\cdot CHMe\cdot COMe,$$

which is obtained as an oil boiling at 155·5° (corr.) under 16 mm. pressure, and having a sp. gr. 0·9560 and n_D 1·51284 at 20°; its *semicarbazone* crystallises in leaflets melting at 148·5° (corr.); the other product of the reduction, *δε-di-γ-cuminyl-γζ-dimethylocta-βη-dione*,

$$C_2H_2(C_6H_4Pr^{\beta})_2(CHMe\cdot COMe)_2,$$

crystallises in rhombic plates melting at 145·5° (corr.).

Since hypochlorous acid oxidises ketones of the type R·CH:CMe·COMe to acids with one carbon atom less, whilst ketones of the type R·CH:CH·COEt are not attacked (compare Stoermer and Wehler, 1903, i, 40), it is possible to distinguish between the α- and γ-cuminylidene compounds; the α-compound is unchanged, but the γ-compound is oxidised to α-methyl-*p*-*iso*propylcinnamic acid (Perkin, Trans., 1877, 31, 791).

V. *Auto-oxidation Products of Carvone*.—[With Arthur Stähler.] (Compare Abstr., 1898, i, 568; and 1901, i, 551.)—When *d*-carvone is oxidised by shaking it up with a solution of barium hydroxide, Δ^8-menthene-2 : 6-dione, $CHMe{<}{\substack{CO\cdot CH_2\\ CO\cdot CH_2}}{>}CH\cdot CMe{:}CH_2$ (m. p. 187—188°, *loc. cit.*), is formed in small quantity; the same diketone is also obtained by oxidising *l*-carvone in a similar manner. The menthenedione is inactive, a fact which is worthy of notice, since, if it were a keto-enolic compound, it would be expected to be optically active. *d*-Carvonehydroxylamino-oxime (compare Harries and Mayrhofer, Abstr., 1899, i, 624), the melting point of which is now found to be 106°, was converted into the dioxime (m. p. 192°. Compare *loc. cit.*), which, on hydrolysis with dilute sulphuric acid, yields Δ^8-menthene-2 : 6-dione. This diketone, which does not combine with phenylcarbimide as does the nearly related methyldihydroresorcinol, is readily converted into the dioxime from which it was formed, and into a *semicarbazone* which forms crystals melting at 235°. Phenylhydrazine reacts with the menthenedione in a complicated manner, giving the *phenylhydrazone* of a phenylazo-compound,

$$CMe{<}{\substack{C({:}N_2HPh)\cdot CH_2\\ C(N_2Ph)\text{——}CH_2}}{>}CH\cdot CMe{:}CH_2,$$

which crystallises in garnet-red needles melting at 147°. 8-*Bromo-*

mentha-2 : 6-dione, prepared by dissolving the menthenedione in a solution of hydrogen bromide in acetic acid, crystallises in leaflets melting at 135°. When boiled with a methyl-alcoholic solution of potassium hydroxide, hydrogen bromide is eliminated, Δ^4-*menthene-2 : 6-dione* being produced, crystallising in long needles melting at 157°. It forms an additive product with hydrogen bromide, which is identical with the 8-bromo-compound.

Δ^8-Menthenedione is also obtained from *l*-carvoneoxamino-oxime; the latter is obtained as crystals melting at 109° by Harries and Mayrhofer's method; its *hydrochloride* is a hygroscopic crystalline powder; its *dibenzoyl* derivative forms prisms melting at 168°, and its *diphenylcarbamide* crystallises in needles melting at 152°. The diphenylcarbamide from *d*-carvoneoxamino-oxime was erroneously described as melting at 97° instead of 161°. On oxidation by the air, the hydroxylamino-oxime is converted into the dioxime (m. p. 188°), which yields a *dibenzoyl* derivative melting at 129° (compare Harries and Mayrhofer, who record the melting point as 118—120°). The dioxime is converted on hydrolysis into the menthenedione.

Eucarvone.—[With Arthur Stähler.] (Compare Baeyer, Abstr., 1894, i, 435; 1898, i, 675.)—*Eucarvonehydroxylamino-oxime*,

$$OH\cdot NH\cdot C_{10}H_{15}\colon N\cdot OH,$$

is prepared by keeping eucarvone and hydroxylamine in methyl-alcoholic solution for eight days, and then, after removal of the solvent, converting the hydroxylamino-oxime into an *oxalate*; an acid and a neutral oxalate are formed, the latter being readily isolated, as it is insoluble in water, melting at 198°; *hydroxylamino-oxime* forms crystals melting at 141—142°. The *picrate* crystallises in yellow needles, and the *diphenylcarbamide* forms crystals melting at 157°. No evidence was obtained for the view that the eucarvone contains a trimethylene ring.

K. J. P. O.

Stereoisomeric Oximes of Dypnone. Ferd. Henrich and A. Wirth (*Ber.*, 1904, 37, 731—734. Compare Delacre, *Bull. Acad. Belg.*, 1890, [iii], 20, 471, and Harries and Gollnitz, preceding abstract).—syn-*Dypnoneoxime*, $\begin{array}{l}CMePh\colon CH\cdot CPh\\ \qquad\qquad\quad \| \\ \qquad\qquad\quad N\cdot OH\end{array}$, prepared by boiling an alcoholic solution of dypnone with hydroxylamine hydrochloride (1 mol.) for 5 hours, crystallises from alcohol in thick plates, melts at 134°, and undergoes the Beckmann transformation, forming *β-methylcinnamoylanilide*, $CMePh\colon CH\cdot CO\cdot NHPh$, which crystallises from dilute alcohol or light petroleum in white leaflets and melts at 121°. When the *syn*-oxime is heated for an hour on the water-bath with concentrated sulphuric acid, it is converted into anti-*dypnoneoxime*, $\begin{array}{l}CMePh\colon CH\cdot CPh\\ \qquad\qquad\quad \| \\ \qquad\qquad OH\cdot N\end{array}$, which is also obtained by heating dypnone with an alcoholic solution of hydroxylamine hydrochloride containing potassium hydroxide; it crystallises from ether in slender, white needles, melts at 78°, and does not undergo the Beckmann transformation.

W. A. D.

Aromatic Ketones. HEINRICH WIELAND (*Ber.*, 1904, 37, 1142—1148. Compare Dimroth, Abstr., 1903, i, 629).—An attempt was made to prepare aromatic hydrocarbons of the allylene series from ketones derived from diphenylpropane by conversion into ketochlorides and removal of hydrogen chloride.

Dibenzyl ketone, prepared by distilling calcium phenylacetate under reduced pressure, reacts with phosphorus pentachloride, forming *β-chloro-αγ-diphenylpropylene*, $CH_2Ph\cdot CCl{:}CHPh$, a yellow oil, boiling at 181° under 12 mm. pressure, together with small quantities of crystalline products. Potassium hydroxide in methyl alcohol converts the chloro-compound into a hydrocarbon, $C_{15}H_{12}$, which crystallises from alcohol as a bulky, white powder, becoming yellow in the air, and melts at 121·5°. It may be diphenylallylene, $CHPh{:}C{:}CHPh$, or phenylbenzylacetylene, $CPh{:}C\cdot CH_2Ph$, but the quantity obtained was too small for a study of its reactions.

Diisonitrosodibenzyl ketone, $CO(CPh{:}N\cdot OH)_2$, prepared by the action of sodium and amyl nitrite on dibenzyl ketone, crystallises from chloroform in bright green leaflets and melts at 133·5°.

Dibenzyl ketone and cinnamaldehyde condense in presence of a small quantity of diethylamine to 2 : 5 : 6-*triphenyl*cyclo-Δ^2-*hexene*-1-*one*, $\begin{matrix} CPh\cdot CO\cdot CHPh \\ | \qquad\qquad | \\ CH\cdot CH_2\cdot CHPh \end{matrix}$, which separates from alcohol in colourless crystals, melts and decomposes at 181—191°, and dissolves sparingly in alcohol, ether, or light petroleum, readily in benzene or chloroform; it decolorises potassium permanganate and yields a waxy additive product with bromine. Tin and hydrochloric acid do not reduce it, but convert it into an *isomeride*, crystallising from alcohol in colourless needles and melting at 136°; it is more soluble than the former compound.

Benzylideneacetophenone polymerises under the influence of acetic anhydride and sulphuric acid, forming a dimolecular compound, which crystallises from alcohol in glistening, white needles and melts at 134°. It does not take up bromine, and is probably a tetramethylene derivative, $\begin{matrix} CHPh\cdot CH\cdot CO\cdot Ph \\ | \qquad | \\ CHPh\cdot CH\cdot CO\cdot Ph \end{matrix}$. C. H. D.

***p*-Nitrodibenzoylmethane.** HEINRICH WIELAND (*Ber.*, 1904, 37, 1148—1152).—The course of the reaction by which dibromides containing the group $-CHBr\cdot CHBr-$ are converted into the corresponding ketones $-CO\cdot CH_2-$ has been explained by Thiele and Haeckel (Abstr., 1903, i, 160). In the present paper, an intermediate product has also been isolated confirming this view.

p-Nitrobenzylideneacetophenone dibromide,

$$NO_2\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot COPh,$$

crystallises in nacreous leaflets and melts at 151° (compare Sorge, Abstr., 1902, i, 379). Ammonia converts it into yellow crystals of the corresponding *piperazine*, $\begin{matrix} COPh\cdot CH\cdot NH\cdot CH\cdot COPh \\ | \qquad\qquad | \\ NO_2\cdot C_6H_4\cdot CH\cdot NH\cdot CH\cdot C_6H_4\cdot NO_2 \end{matrix}$, melting at 141° and yielding a crystalline nitrosoamine with nitrous acid.

Potassium hydroxide in methyl-alcoholic solution converts the

dibromide into an *acetal*, $NO_2\cdot C_6H_4\cdot C(OMe)_2\cdot CH_2\cdot COPh$, which crystallises from alcohol in large, colourless tablets and melts at 91°. Acids in the cold, and alkalis on warming, convert it into p-*nitrodibenzoylmethane*, $NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot COPh$, crystallising from alcohol in yellow needles and melting at 160°, dissolving readily in benzene, more sparingly in alcohol or chloroform. The alkali salts are precipitated from alcohol in orange scales. Ferric chloride produces a red coloration, copper acetate precipitates a yellow copper salt. Hydroxylamine forms p-*nitrodiphenylisooxazole*,

$$\begin{array}{l} NO_2\cdot C_6H_4\cdot \overset{}{C}\cdot CH{:}CPh \\ \qquad\qquad\;\; N \text{———} O \end{array},$$

which crystallises from glacial acetic acid in glistening, yellow leaflets, sparingly soluble in all solvents, and melts at 221°.

Hydrazine yields p-*nitrodiphenylpyrazole*, $\begin{array}{l} NO_2\cdot C_6H_4\cdot C\cdot CH{:}CPh \\ \qquad\qquad\;\; N \text{———} NH \end{array}$,
which forms silky, yellow needles and melts above 250°. Reduction yields the *amino*-base melting at 179°; the *hydrochloride* chars at 235°.

Phosphorus pentachloride converts *p*-nitrodibenzoylmethane into α-*chloro*-ω-p-*nitrobenzoylstyrene*, $NO_2\cdot C_6H_4\cdot CO\cdot CH{:}CClPh$ or

$$NO_2\cdot C_6H_4\cdot CCl{:}CH\cdot COPh,$$

which crystallises from methyl alcohol in yellow tablets and melts at 131°. C. H. D.

Condensation Products from Anthraquinone-β-sulphonic Acid and Primary Aromatic Amines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 147277).—Condensation products are obtained on heating anthraquinone-β-sulphonic acid with primary aromatic amines, preferably in presence of a condensing agent, such as boric acid, and of a reducing agent, such as stannous chloride. The *compound* from anthraquinone-2-sulphonic acid and aniline crystallises from pyridine in orange needles and dissolves in hot alcohol or acetic acid. The solution in concentrated sulphuric acid is yellow, and has an intense blue fluorescence, which disappears on heating. Similar products are obtained from *o*-toluidine and *m*-xylidine. C. H. D.

Nitro-nitroamines and Nitroamines of the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 146848 and 148109).—The action of nitric acid in limited quantity on diamino- or dialphyldiamino-anthraquinones and their sulphonic acids leads to substitution in the anthraquinone ring, an excess of nitric acid reacts with the amino- or imino-groups present, forming nitroamines, containing the group $-NH\cdot NO_2$ or $-N(alphyl)\cdot NO_2$. These nitroamines are unstable and explosive, and the nitro-group is partially or entirely eliminated from them on boiling with nitrobenzene, aromatic hydrocarbons, or other indifferent solvents, or by the action of phenols or aminoanthraquinones in concentrated sulphuric acid at the ordinary temperature.

1 : 5-Diaminoanthraquinone yields dinitrodiamino-, tetranitrodiamino-, or tetranitrodinitroamino-anthraquinone on nitration, ac-

cording to the quantity of nitric acid employed. Tetrabromo-1 : 5-diaminoanthraquinone yields only tetrabromodinitroaminoanthraquinone, no nitration taking place in the ring. When a mixture of sulphuric and nitric acids is employed, sulphonation also occurs. The patent contains the colour-reactions of a large number of nitration products.

Dibromodinitro-1 : 5-*diaminoanthraquinone*, prepared by heating dibromodinitro-1 : 5-dinitroaminoanthraquinone with phenol or cuminol, crystallises from phenol or nitrobenzene in green, metallic needles, melts above 300°, and forms red solutions. Sodium sulphide reduces it to an indigo-blue *dibromotetraminoanthraquinone*. *Nitro-β-aminoanthraquinone* is a yellow, insoluble powder.

Tetranitro-1 : 5-*diaminoanthraquinone*, prepared from tetranitro-1 : 5-dinitroaminoanthraquinone and 1 : 5-diaminoanthraquinone in cold concentrated sulphuric acid solution, is a dark violet powder, which decomposes on heating. *Tetrabromo*-1 : 5-*diaminoanthraquinone*, which may be prepared by saturating an alcoholic solution of tetrabromo-1 : 5-dinitroaminoanthraquinone with hydrogen chloride and heating, separates in red crystals. C. H. D.

1-Nitro-5- and -8-aminoanthraquinones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 147851).—Dinitroanthraquinones have not hitherto been partially reduced to nitroaminoanthraquinones, but this reduction may be effected by heating with aromatic mono- or di-alkylamines. Thus, on boiling 1 : 5-dinitroanthraquinone with dimethylaniline or similar base, a blood-red solution is obtained, from which 1-*nitro*-5-*aminoanthraquinone* separates in garnet-red prisms on cooling. It dissolves in fuming sulphuric acid to a reddish-violet solution, 1-*nitro*-8-*aminoanthraquinone* forms a yellow solution. The constitution of these compounds is confirmed by reduction to diaminoanthraquinones, and by conversion into dihydroxyanthraquinones. C. H. D.

[Arylaminoanthraquinones.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 148767. Compare Abstr., 1902, i, 476).—The acyl derivatives of 4-nitro-1-aminoanthraquinones condense with aromatic amines more readily than the free bases, and the acyl group may then be readily removed by means of acids.

1-*Acetylamino*-4-p-*toluidinoanthraquinone*, from 1-acetylamino-4-nitroanthraquinone and *p*-toluidine, crystallises from pyridine in broad, dark-violet needles with greasy lustre and melts at 193°. It is insoluble in water, but dissolves in organic solvents. The *compound* from 1 : 5-diacetylamino-4 : 8-dinitroanthraquinone and aniline is bluish-violet and melts and decomposes above 300°. The solution in concentrated sulphuric acid is colourless, and hydrolysis occurs gradually. C. H. D.

Preparation of Leucohydroxyanthraquinones. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 148792).—The reduction of 4-nitro-1-hydroxyanthraquinone derivatives or of 4-nitro-1-aminoanthraquinones in acid solution with an excess of reducing agent pro-

duces leuco-compounds in which the amino-group is very readily replaced by hydroxyl on heating. In the case of ethers, the ether group is removed. Sulpho-groups or halogen atoms, if present in the same ring as the nitro-radicle and the hydroxy- or amino-group, are also replaced by hydrogen. The leucohydroxyanthraquinones are yellow or brown, and dissolve in alkalis to yellow solutions, oxidising in contact with air. The appearance and colour-reactions of a number of leuco-compounds are described. C. H. D.

Preparation of Amino-5- and -8-hydroxyanthraquinones. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 148875).—1-Aminoanthraquinone-5- and -8-sulphonic acids, prepared by successive nitration and reduction of anthraquinone-α-sulphonic acid, may be separated by means of dilute acetic acid, in which the 1 : 5-compound is the more soluble. Heating with hydroxides of the alkali earths under pressure converts them into 1-*amino*-5-*hydroxyanthraquinone*, crystallising from benzene in red, metallic prisms, melting at 210°, and dissolving sparingly in water, but more readily in alcohol or acetone, and 1-*amino*-8-*hydroxyanthraquinone*, crystallising from benzene in long, brown needles and melting at 230°. The 1 : 5-compound forms an *acetyl* derivative, crystallising in needles, and a *diacetyl* derivative, forming yellow, glistening leaflets. Fusion with oxalic acid forms an *oxamic acid* crystallising in yellow prisms. C. H. D.

Metal-organic Syntheses of the Acyl Camphors. Julius W. Brühl (*Ber.*, 1904, 37, 746—761).—Claisen's method of preparing formylcamphor (hydroxymethylenecamphor) by the action of sodium on a mixture of camphor and an alkyl formate gives only traces of acetylcamphor when the alkyl formate is replaced by an alkyl acetate. Forster's method for preparing benzoylcamphor also cannot be used for the preparation of acetylcamphor, as this compound is only produced in small quantities when acetic anhydride, chloride, or bromide is allowed to act on sodium camphor; the main products of the action when acetyl chloride is allowed to act on sodium camphor are bornyl acetate and the acetate of enolic camphor; these were not separated, but their presence was indicated by the formation of both borneol and camphor by alkaline hydrolysis.

In confirmation of Malmgren's observations, it has been found (1) that magnesium acts on bromocamphor in ethereal solution, giving two magnesium-organic compounds, one soluble and the other insoluble in ether; (2) that a similar action takes place in boiling xylene solution; no hydrogen is liberated, although a certain amount of hydrogen bromide is eliminated from the bromocamphor, and the products are camphor, borneol, and Oddo's dicamphoquinone, $(C_{10}H_{14}O)_2$; (3) that the magnesium compound gives camphocarboxylic acid when acted on by carbon dioxide, acetylcamphor, and (?) acetylcamphenol acetate, $C_8H_{14}<\begin{matrix}CAc\\ \|\\ COAc\end{matrix}$. The insoluble magnesium-organic compound is probably not a mixture of magnesium camphor and magnesium bromide, $(C_{10}H_{15}O)_2Mg,MgBr_2$, as Malmgren supposed, for magnesium bromide forms soluble ether compounds, but may be regarded as the enolic

magnesium compound, $C_8H_{14}<\begin{matrix}CH \\ \| \\ C\cdot OMgBr\end{matrix}$. Whilst the magnesium-organic compounds of iodo- and bromo-camphocarboxylic esters yield carbon-ethers with acetyl haloids and only oxygen-ethers with acyl esters, the magnesium compound from bromocamphor gives acylcamphors by the action of acyl haloids, and an even simpler method of preparing acetylcamphor consists in allowing magnesium (1 atom) to act on a solution of bromocamphor (1 mol.) in an excess of ethyl acetate; the acetylcamphor is extracted by means of soda, and the tertiary carbinol and camphor remain in the insoluble layer; the yield of acetylcamphor, when using acetyl chloride or bromide, is at the most 8 per cent., but, when using methyl or ethyl acetate, may be as much as 20 or 21 per cent. of the theoretical quantity (Malmgren obtained 37 per cent.).

Camphocarboxylic acid could not be obtained by the action of zinc on bromocamphor in presence of carbon dioxide, but a very favourable yield of acetylcamphor was obtained by using zinc.

The best results are obtained in ethereal solution; the yield, with granulated zinc, bromocamphor, and ethyl acetate, was 16—17 per cent. in ethereal solution, and 9—10 per cent. in xylene solution; by using zinc dust in place of granulated zinc, the yield in ethereal solution was raised to 35 per cent.; a yield of 14—15 per cent. was obtained from iodocamphor and ethyl acetate in xylene.

$\alpha\alpha'$-Dibromocamphor gave, with magnesium and ethyl acetate, α-bromocamphor, acetylcamphor, and acetylcamphenol acetate, but no $\alpha\alpha'$-diacetylcamphor.

Bromoformylcamphor is also reduced in a similar manner to hydroxymethylenecamphor. T. M. L.

Chemical and Physical Properties and Constitution of the Acylcamphors. JULIUS W. BRÜHL (*Ber.*, 1904, 37, 761—773).—The boiling points of the series are:

	B. p.	Pressure.
Hydroxymethylenecamphor ...	105°	11·0 mm.
Acetylcamphor	118—118·5	11·2 ,,
,, ...	127—128	15·5 ,,
Propionylcamphor*	129	11·0 ,,
Butyrylcamphor*	132—133	11·2 ,,
,, ...	134—135	12·0 ,,
*iso*Valerylcamphor	141—148	11·0 ,,

Only the first member of the series is solid. It has a camphor-like smell, whilst the odour of acetylcamphor resembles rather that of menthol; the higher homologues have a feebler and less characteristic odour, but still suggestive of menthol.

Hydroxymethylenecamphor liberates acetic acid from its salts, dissolves in the calculated quantity of sodium hydroxide solution, and also dissolves in sodium carbonate and even in sodium hydrogen

* Malmgren's boiling points are about 10° higher.

carbonate; acetylcamphor is much less acid; acetylcamphor also dissolves in the calculated quantity of aqueous sodium hydroxide, but the solution is strongly alkaline and becomes cloudy as it absorbs carbon dioxide from the air. When titrated with sodium hydroxide and phenolphthalein, the colour appeared when 18 per cent. of the theoretical amount of normal, and 20 per cent. of decinormal, sodium hydroxide still remained to be added; with litmus and decinormal sodium hydroxide, the end-point was reached when only 21 per cent. of the theoretical amount of alkali had been added. Acetylcamphor is soluble in sodium carbonate solution, but requires 13 times the theoretical quantity of alkali. It can, however, still be readily extracted from ether by means of alkalis. Propionylcamphor also dissolves in the calculated quantity of sodium hydroxide solution, but gives a coloration with phenolphthalein and sodium hydroxide when only 54 per cent. of the theoretical quantity of alkali is added; it no longer acts on blue litmus, but can be extracted from ethereal solution by twice normal sodium hydroxide. Butyrylcamphor is still less acid in its properties, and can only be extracted with difficulty from its ethereal solution by twice normal sodium hydroxide, whilst valerylcamphor requires 50 per cent. potassium hydroxide for this purpose, and can then be only extracted partially.

Hydroxymethylenecamphor forms an acid and a normal copper salt, acetylcamphor only a *normal copper* salt, which crystallises from light petroleum in glistening, dark olive-green flakes and melts at 201—202°. The higher homologues also form only the normal copper salts.

The sp. gr., mol. vol., refractive index for the three hydrogen lines and the D line, molecular refraction, and dispersion are tabulated in the original paper for acetylcamphor, propionylcamphor, butyrylcamphor, and *iso*valerylcamphor.

The conclusion is drawn that all the members of the series exist exclusively, like hydroxymethylene camphor, in the keto-enolic form, as hydroxyalkylidene compounds, $C_8H_{14}<\begin{matrix}C{:}CR{\cdot}OH\\ |\\ CO\end{matrix}$. T. M. L.

Anhydrohydroxylamine Unsaturated Ketones. FRIEDERICH W. SEMMLER (*Ber.*, 1904, **37**, 950—957).—On heating pulegonehydroxylamine with concentrated acids at from 50—100°, amongst other products, a weak base, *a-anhydropulegonehydroxylamine*, $C_{10}H_{17}ON$, is formed. This boils at 91° under 8 mm. pressure, has a sp. gr. 0·9731 at 20°, a_D in a 10 mm. tube $+37°10'$, $n_D = 1·4757$, so that the molecular refraction is 48·38 indicating the presence of a dicyclic system in the compound. It shows most of the reactions of the alkaloids. The *oxime*, $C_{10}H_{17}N{:}N$, melts at 181°, and is soluble both in acids and alkalis; the *semicarbazone*, $C_{10}H_{17}N{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, melts at 153—154°; the *benzenesulphonyl base*, $C_6H_5SO_2{\cdot}C_{10}H_{16}NO$, which melts at 120°, and is insoluble even in concentrated alkali; the *methyl base*, $C_{10}H_{16}MeON$, boils at 102—104° under 9 mm. pressure, has a sp. gr. 0·968 at 20°, and n_D 1·480, and forms a *picrate* melting at 170°. These reactions point to the compound being a saturated ketoimine base.

On reduction with sodium and alcohol, a *tetrahydro-base*, $C_{10}H_{21}ON$, is formed which boils at 134—135° under 18 mm. pressure, has a sp. gr. 0·9646 at 20°, and $n_D = 1·4815$. It does not form a sparingly soluble picrate. When zinc dust and hydriodic acid were used for the reaction, a *base*, $C_{10}H_{19}ON$, was formed, boiling at 106° under 11 mm. pressure and having a sp. gr. 0·952 at 20°; this gave a thiocarbamide melting at 201°. The base, $C_{10}H_{17}ON$, forms a *thiocarbamide*, $NHPh·CS·N:C_{10}H_{16}O$, melting at 134°, and a *picrate* melting at 152°.

E. F. A.

Thujyl Derivatives. Iwan L. Kondakoff and V. Skworzoff (*J. pr. Chem.*, 1904, 69, 176—186. Compare Abstr., 1902, i, 807; 1903, i, 642).—Thujene, when treated with halogen acids, gives a certain quantity of liquid dihalogen compounds; this is probably formed from *iso*thujene present; the yield is small when the thujene has been prepared by the xanthate method, but considerable in the case of thujene prepared from thujyl haloids. In the latter case, the dibromide, as well as the dichloride, was treated with aqueous alcohol; after half a year, no formation of a terpin had occurred (von Baeyer, Abstr., 1894, i, 92). The main product, $C_{10}H_{18}Br_2$, boiled at 134—135° under 11 mm. pressure, and lost 2HBr when heated with alcoholic potassium hydroxide at 120°, yielding a hydrocarbon that boiled at 179—185° and had a sp. gr. 0·8449 at 18°/4°, n_D 1·48074, and $[\alpha]_D - 0°38'$.

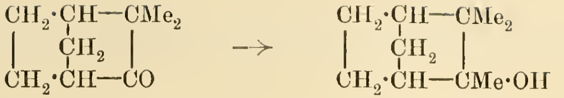
The author defends his formula for thujone (Abstr., 1902, i, 807) against the criticisms of Tschugaeff (*Chem. Zeit.*, 1903, 27, 970) and Semmler (*Ber.*, 1903, 36, 4367).

C. F. B.

Camphene. Georg Wagner, St. Moycho, and Fr. Zienkowski (*Ber.*, 1904, 37, 1032—1037).—Large quantities of camphene were oxidised by 4 per cent. aqueous potassium permanganate at 60°, the neutral products isolated being camphenylone, campheneglycol, and a *compound*, $C_{10}H_{16}O_2$; the acid products are camphenecamphoric acid and camphenylic acid. The *compound*, $C_{10}H_{16}O_2$, crystallises from ether in beautiful plates, melts at 169—170°, and is indifferent to hydroxylamine, semicarbazide, and Fehling's solution; on further oxidation with potassium permanganate, it gives a *ketone* which is volatile with steam, and yields a *semicarbazone* melting at 184·5°, together with two *acids* having the composition $C_{10}H_{14}O_3$ and $C_{10}H_{16}O_4$, melting respectively at 197—198° and 203°. The oxidation products of the compound $C_{10}H_{16}O_2$ are thus quite different from those of campheneglycol. Campheneglycol when pure melts at 199—200°.

Small quantities of the unchanged hydrocarbon cyclene, $C_{10}H_{16}$ (Wagner and Godlewski, *J. Russ. phys. Chem. Soc.*, 1897, 29, 121), remain after the whole of the camphene has been oxidised; it is probable, therefore, that the dehydrating action of zinc chloride on *iso*borneol gives rise, in addition to camphene, to a small quantity of cyclene.

Assuming Wagner's formulæ, camphenylone should give *iso*borneol when treated with methyl iodide and magnesium, thus:



Actually, however, a new *alcohol*, $C_{10}H_{17}\cdot OH$, is formed, which crystallises from light petroleum, melts at 117·5—118°, boils and partially decomposes at 204—206°, and with phenylcarbimide gives a *urethane* which melts at 127·5—128°. With glacial acetic acid and sulphuric acid, it gives a mixture of camphene and, probably, *iso*bornyl acetate. It is apparently optically inactive. W. A. D.

New Constituents of Oil of Roses. HUGO VON SODEN and WALTER TREFF (*Ber.*, 1904, 37, 1094—1095. Compare Abstr., 1901, i, 39, 733).—Some 5—10 per cent. of nerol (Abstr., 1903, i, 267) has been obtained from oil of roses; it is slightly optically active owing to the presence of small amounts of citronellal (?). About 1 per cent. of eugenol and a *sesquiterpene alcohol*, $C_{15}H_{26}O$, have also been isolated; the latter distils at 149° under 4 mm. pressure, has a sp. gr. 0·894 at 15°, is optically inactive, and closely resembles farnesol. J. J. S

Blue Dyes of the Anthracene Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 145237).—The disulphonic acids of dinitroanthrachrysone dialkyl ethers (Abstr., 1903, i, 840) may be reduced by stannous chloride or sodium sulphide to diaminoanthrachrysone dialkyl ether disulphonic acids, which form dark blue, crystalline alkali salts, dissolving in water to pure blue solutions, becoming greenish-blue on addition of alkali hydroxides. The salts dissolve in concentrated sulphuric acid to orange-coloured solutions, becoming blue on dilution with water. C. H. D.

Brown Colouring Matter of Algæ (Phycophain and Phycoxanthin). N. GAIDUKOV (*Chem. Centr.*, 1904, i, 667; from *Ber. Deutsch. bot. Ges.*, 21, 535—539).—The position of the absorption band of phycophain, the brown colouring matter of the *Phaeophyceæ*, observed by Hansen (*Arb. Bot. Inst. Würzburg*, 3, No. 11) between the lines *b* and *F*, has been quantitatively determined. The fact that the brown colour of the alcoholic extract of the brown and bluish-green algæ is not due to the presence of another dye, phycoxanthin, but depends entirely on the solubility of phycophain, has also been confirmed. Phycophain is not only soluble in boiling, but also in cold, water, and in dilute alcohol, hence, whilst a 97 per cent. solution of alcohol extracts the dye from the wet algæ, it fails to do so from the dry. Phycoxanthin is a mixture of phycophain and carotin, or of chlorophyll and carotin. The author terms phycophain "brown phycochrome," and by a change of definition "phycochrome Nägeli" is relegated to the phycochrome groups to which the chromatophores of the dead algæ and chlorophyll and carotin also belong. The dyes isolated from the algæ are not always identical with those of the chromatophores, thus the green fluorescence of the aqueous extract of *Dictyota dichotoma*, which in the living state is fluorescent and has an absorption band at λ545, soon disappears after

filtration, and the brown dye contained in the extract shows the absorption bands of phycophain. Phycophain is also contained in the rhodophyceæ. E. W. W.

Synthesis of 2-Hydroxyflavonol. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1904, **37**, 773—778).—*Quinacetophenone monomethyl ether*, $OMe\cdot C_6H_3(OH)\cdot COMe$, prepared by the action of sodium hydroxide on a mixture of quinacetophenone and methyl sulphate, crystallises from dilute alcohol in pale yellow crystals and melts at 52°. When treated with sodium hydroxide and benzaldehyde, it yields 6-*methoxyflavanone*, $OMe\cdot C_6H_3<\begin{matrix}O-CHPh\\ CO\cdot CH_2\end{matrix}$, which crystallises from alcohol in white needles and melts at 141—142°; its solution in dilute alcohol shows a blue fluorescence. 3-iso*Nitroso*-6-*methoxyflavanone*, $OMe\cdot C_6H_3<\begin{matrix}O-CHPh\\ CO\cdot C:NOH\end{matrix}$, prepared by the action of amyl nitrite on the preceding compound, crystallises from benzene in yellow needles and melts and decomposes at 160°.

6-*Methoxyflavonol*, $OMe\cdot C_6H_3<\begin{matrix}O-CPh\\ CO\cdot C\cdot OH\end{matrix}$, prepared by hydrolysing the preceding oxime, crystallises from alcohol in pale yellow needles and melts at 204—205°; it forms a sparingly soluble, yellow sodium salt like the 1-hydroxyflavones, and colours mordanted cotton exactly in the same manner as kaempferide and kaempferol (Abstr., 1889, 868); when boiled down with 50 per cent. potassium hydroxide, it is decomposed, yielding quinol and benzoic acid. The *acetyl* derivative, $OMe\cdot C_6H_3<\begin{matrix}O-CPh\\ CO\cdot C\cdot OAc\end{matrix}$, crystallises from alcohol in stout, pure white needles, and melts at 164—166°.

6-*Ethoxyflavonol*, $OEt\cdot C_6H_3<\begin{matrix}O-CPh\\ CO\cdot C\cdot OH\end{matrix}$, crystallises from alcohol in yellow spangles and melts at 177—178°. Its *acetyl* derivative, $C_{19}H_{16}O_5$, crystallises from dilute alcohol in colourless needles and melts at 133—134°.

6-*Hydroxyflavonol*, $OH\cdot C_6H_3<\begin{matrix}O-CPh\\ CO\cdot C\cdot OH\end{matrix}$, prepared by the action of hydriodic acid on the methyl ether, crystallises from 50 per cent. alcohol in colourless needles, melts at 233—234°, and yields a greenish-yellow solution in alkali hydroxides. The *diacetyl* derivative, $C_{19}H_{14}O_6$, crystallises from alcohol in colourless needles and melts at 195—196°. The *dimethyl ether*, $C_{17}H_{14}O_4$, crystallises from alcohol in colourless, silky needles, and melts at 128—129°. T. M. L.

Synthesis of an Isomeride of Fisetin. STANISLAUS VON KOSTANECKI and S. KUGLER (*Ber.*, 1903, **37**, 779—781).—6 : 3′ : 4′-*Trimethoxyflavanone*, $OMe\cdot C_6H_3<\begin{matrix}O-CH\cdot C_6H_3(OMe)_2\\ CO\cdot CH_2\end{matrix}$, prepared by the action of sodium hydroxide on quinacetophenone monomethyl ether

veratraldehyde, crystallises from alcohol in colourless spangles and melts at 175—176°. The iso*nitroso*-derivative,

$$OMe\cdot C_6H_3<\begin{matrix}O-CH\cdot C_6H_3(OMe)_2\\ CO\cdot C{:}N\cdot OH\end{matrix},$$

crystallises from benzene in yellow needles and melts and decomposes at 168°. 6 : 3′ : 4′-*Trimethoxyflavonol*,

$$OMe\cdot C_6H_3<\begin{matrix}O-C\cdot C_6H_3(OMe)_2\\ CO\cdot C\cdot OH\end{matrix},$$

prepared by hydrolysing the preceding oxime, crystallises from alcohol in minute, pale-yellow needles and melts at 189—190°. The *acetyl* derivative, $C_{20}H_{18}O_7$, crystallises from dilute alcohol in rosettes of small, colourless needles and melts at 140—141°. 6 : 3′ : 4′-*Trihydroxyflavonol*, $OH\cdot C_6H_3<\begin{matrix}O-C\cdot C_6H_3(OH)_2\\ CO\cdot C\cdot OH\end{matrix}$, isomeric with fisetin, prepared by the action of hydriodic acid on the trimethyl ether, crystallises from alcohol in minute, yellow needles, melts and decomposes at 335°, and dyes cotton orange-yellow with aluminium, and olive-brown with iron mordants. The *tetra-acetyl* derivative, $C_{23}H_{18}O_{10}$, forms colourless needles, melts at 197—198°, and is sparingly soluble in alcohol. T. M. L.

Synthesis of 2 : 4′-Dihydroxyflavonol. STANISLAUS VON KOSTANECKI and M. L. STOPPANI (*Ber.*, 1904, 37, 781—784).—6 : 4′-*Dimethoxyflavanone*, $OMe\cdot C_6H_3<\begin{matrix}O-CH\cdot C_6H_4\cdot OMe\\ CO\cdot CH_2\end{matrix}$, prepared from quinacetophenone monomethyl ether and anisaldehyde, crystallises from alcohol in long, colourless needles and melts at 160°; its alcoholic solution shows a blue fluorescence. The iso*nitroso*-derivative,

$$OMe\cdot C_6H_3<\begin{matrix}O-CH\cdot C_6H_4\cdot OMe\\ CO\cdot C{:}N\cdot OH\end{matrix},$$

prepared by the action of amyl nitrite on the preceding compound, crystallises from benzene in yellow needles and melts and decomposes at 157—158°.

6 : 4′-*Dimethoxyflavonol*, $OMe\cdot C_6H_3<\begin{matrix}O-C\cdot C_6H_4\cdot OMe\\ CO\cdot C\cdot OH\end{matrix}$, prepared by hydrolysing the preceding oxime, crystallises from alcohol in pale yellow needles and melts at 184—185°; it is insoluble in cold sodium hydroxide, but on warming forms a deep yellow, very sparingly soluble, sodium derivative. The *acetyl* derivative, $C_{19}H_{16}O_6$, crystallises from dilute alcohol in colourless, silky needles and melts at 131—132°.

6 : 4′-*Dihydroxyflavonol*, $OH\cdot C_6H_3<\begin{matrix}O-C\cdot C_6H_4\cdot OH\\ CO\cdot C\cdot OH\end{matrix}$, prepared by the action of hydriodic acid on the dimethyl ether, crystallises from alcohol in bright yellow needles and melts and decomposes at 340°. The *triacetyl* derivative, $C_{21}H_{16}O_8$, crystallises from alcohol in rosettes of long, white needles and melts at 169°. T. M. L.

Synthesis of Fisetin. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and JOSEF TAMBOR (*Ber.*, 1904, 37, 784—791).—7-*Ethoxy-*

3′ : 4′-*dimethoxyflavanone*, $OEt\cdot C_6H_3{<}\begin{matrix}O{-}CH\cdot C_6H_3(OMe)_2\\ CO\cdot CH_2\end{matrix}$, prepared by the action of 10 per cent. sulphuric acid on an alcoholic solution of 2′-hydroxy-4′-ethoxy-3 : 4-dimethoxychalkone,

$$OEt\cdot C_6H_3(OH)\cdot CO\cdot CH{:}CH\cdot C_6H_3(OMe)_2,$$

crystallises from alcohol in colourless, flat prisms, melts at 110°, and dissolves with an orange-yellow colour in alcoholic potassium hydroxide. Its iso*nitroso*-derivative, $OEt\cdot C_6H_3{<}\begin{matrix}O{-}CH\cdot C_6H_3(OMe)_2\\ CO\cdot C{:}N\cdot OH\end{matrix}$, crystallises from benzene in pale yellow, almost colourless needles and melts and decomposes at 175—176°. 7-*Ethoxy*-3′ : 4′-*dimethoxyflavonol*,

$$OEt\cdot C_6H_3{<}\begin{matrix}O{-}C\cdot C_6H_3(OMe)_2\\ CO\cdot C\cdot OH\end{matrix},$$

crystallises from much alcohol in bright yellow, glistening, broad needles and melts at 193—194°. Its *acetyl* derivative, $C_{21}H_{20}O_7$, crystallises from dilute alcohol in colourless needles and melts at 162—163°. The 7 : 3′ : 4′-*trihydroxyflavonol*,

$$OH\cdot C_6H_3{<}\begin{matrix}O{-}C\cdot C_6H_3(OH)_2,H_2O\\ CO\cdot C\cdot OH\end{matrix},$$

prepared by the action of hydriodic acid on the ethyl dimethyl ether, proved to be identical with fisetin, and gave the same tetra-acetyl derivative. T. M. L.

Synthesis of 6 : 3′-Dihydroxyflavonol. STANISLAUS VON KOSTANECKI and ADOLF OTTMANN (*Ber.*, 1904, 37, 957—960).—6 : 3′-*Dimethoxyflavanone*, $OMe\cdot C_6H_4{<}\begin{matrix}O{-}CH\cdot C_6H_4\cdot OMe\\ CO\cdot CH_2\end{matrix}$, prepared by the action of sodium hydroxide on a mixture of quinacetophenone methyl ether and *m*-methoxybenzaldehyde, crystallises in colourless plates melting at 104°; its alcoholic solution has a blue fluorescence, and it dissolves in concentrated sulphuric acid with an orange-red coloration. The iso*nitroso*-derivative crystallises in yellow needles melting and decomposing at 153—154°; it produces a red shade with cobalt mordants and a yellow with uranium, cadmium, and lead mordants owing to the presence of the colouring complex, $O{:}C\cdot C{:}N\cdot OH$.

6 : 3′-*Dimethoxyflavonol*, prepared by heating *iso*nitrosodimethoxyflavanone dissolved in glacial acetic acid with dilute sulphuric acid, crystallises in light yellow, prismatic needles melting at 144°; it is insoluble in cold dilute sodium hydroxide, but on warming, a deep yellow, sparingly soluble *sodium* salt is precipitated. It gives yellow shades with aluminium mordants. The *acetyl* derivative crystallises from dilute alcohol in long, white plates melting at 134°. 6 : 3′-*Dihydroxyflavonol*, $OH\cdot C_6H_4{<}\begin{matrix}O{-}C\cdot C_6H_4\cdot OH\\ CO\cdot C\cdot OH\end{matrix}$, crystallises from alcohol in bright yellow needles and melts and decomposes at 300°; it gives bright yellow shades with aluminium and faint brown shades with iron mordants. The corresponding *triacetyl* derivative crystallises in colourless needles melting at 126—127°. E. F. A.

Synthesis of 7-Hydroxyflavonol. Stanislaus von Kostanecki and M. L. Stoppani (*Ber.*, 1904, 37, 1180—1182).—7-*Methoxyflavanone*, $OMe\cdot C_6H_3<{O-CHPh \atop CO\cdot CH_2}$, prepared by the action of sulphuric acid on 2′-hydroxy-4-methoxychalkone (compare Abstr., 1899, i, 368), crystallises in colourless needles melting at 91°, which dissolve in concentrated sulphuric acid with a greenish-yellow, and in alcoholic sodium hydroxide with an orange-yellow, coloration. The iso*nitroso*-derivative crystallises in colourless plates melting and decomposing at 188°; it gives orange shades with cobalt, and yellow shades with uranium mordants.

7-*Methoxyflavonol*, $OMe\cdot C_6H_3<{O-CPh \atop CO\cdot C\cdot OH}$, crystallises in long, colourless needles melting at 180°; it is insoluble in dilute sodium hydroxide, but forms a yellow, sparingly soluble *sodium* derivative on heating; concentrated sulphuric acid gives rise to a faint yellow coloration and blue fluorescence; with aluminium mordants, bright yellow tints are produced. The *acetyl* derivative forms colourless needles grouped in rosettes, which melt at 140°. 7-*Hydroxyflavonol* crystallises in faintly yellow, almost colourless, prismatic needles, which melt at 257—259° and are easily soluble in dilute sodium hydroxide with a greenish-yellowish coloration. 3-*Acetyl*-7-*acetoxyflavonol*,

$$CH_3CO\cdot OC_6H_3<{O-CPh \atop CO\cdot C\cdot O\cdot COCH_3},$$

forms large, colourless needles which melt at 157°. E. F. A.

Condensation of Hydroxyquinol with Aldehydes. Carl Liebermann and S. Lindenbaum [and, in part, A. Glawe] (*Ber.*, 1904, 37, 1171—1180).—2 : 3 : 7-*Trihydroxy*-9-*phenylfluorone*,

$$CPh<{C_6H_2(OH)_2- \atop C_6H_2O(OH)}>O,$$

prepared by the condensation of benzaldehyde with hydroxyquinol, is an orange-red, crystalline substance very sparingly soluble in organic solvents; the alcoholic solution has a greenish-yellow fluorescence. It dissolves in alkali with a carmine-red coloration, the *potassium* salt dissolves with a purple coloration in water. It gives orange-red shades with aluminium and greyish-violet with iron mordants; the *sulphate*, $C_{19}H_{12}O_5,H_2SO_4$, crystallises with a molecule of ethyl acetate forming gold, glistening platelets. 2 : 3 : 7-*Triacetoxy*-9-*phenylfluorone* crystallises in orange-yellow needles melting at 230—233°. Hydroxyquinol condenses with formaldehyde yielding *methylenebishydroxyquinol*, $CH_2[C_6H_2(OH)_3]_2$, which crystallises in silvery, glistening needles melting at 227—230°, and forming an *acetate*, $C_{13}H_6O_6Ac_6$, which crystallises in colourless, glistening prisms and melts at 152—155°.

2 : 3 : 7-*Trihydroxy*-9-*methylfluorone*, $CMe<{C_6H_2(OH)_2- \atop C_6H_2O(OH)}>O$, produced by condensing hydroxyquinol with para-aldehyde in presence of sulphuric acid, is a red powder sparingly soluble in water; the alcoholic solution and also that in concentrated sulphuric acid are yellow,

and have a yellowish-green fluorescence. With the ordinary oxidising mordants, yellow shades are produced.

Colourless condensation products are produced by the condensation of benzaldehyde with pyrogallol, resorcinol, or phloroglucinol.

E. F. A.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. II. RUDOLF ANDREASCH and ARTHUR ZIPSER (*Monatsh.*, 1904, 25, 159—180. Compare Abstr., 1903, i, 855).—3-Phenylrhodanic acid is most conveniently prepared by von Braun's method (Abstr., 1903, i, 13). Boiling with alkali or barium hydroxide hydrolyses it, forming diphenylthiocarbamide and thioglycollic acid: $2C_9H_7ONS_2 + 4H_2O = 2C_2H_4O_2S + H_2S + CO_2 + CS(NHPh)_2$.

3-*Phenyl*-5-m-*nitrobenzylidenerhodanic acid*,

$$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO{\cdot}NPh}\\ \mathrm{S{-}CS}\end{array},$$

from phenylrhodanic acid and *m*-nitrobenzaldehyde, crystallises from alcohol in bright yellow scales with faint blue reflex, melts at 240° (uncorr.), and dissolves readily in acetone, hot alcohol, or ether, sparingly in glacial acetic acid.

5-m-*Nitrobenzylidene-3-allylrhodanic acid*,

$$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO{\cdot}N{\cdot}C_3H_5}\\ \mathrm{S{-}CS}\end{array},$$

crystallises in yellow, microscopic plates and melts at 145°.

3-*Phenyl*-5-p-*nitrobenzylidenerhodanic acid* forms small, yellow needles dissolving very sparingly in cold acetone, more readily on warming, and blackens at 240° without melting.

5-p-*Nitrobenzylidene-3-allylrhodanic acid* forms golden-yellow scales and melts at 153°.

3-*Phenyl*-5-p-*hydroxy*-m-*methoxybenzylidenerhodanic acid*,

$$\mathrm{OMe{\cdot}C_6H_3(OH){\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO{\cdot}NPh}\\ \mathrm{S{-}CS}\end{array},$$

from phenylrhodanic acid and vanillin, crystallises in very slender, yellow needles and melts at 193°.

5-p-*Hydroxy*-m-*methoxybenzylidene-3-allylrhodanic acid*,

$$\mathrm{OMe{\cdot}C_6H_3(OH){\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO{\cdot}N{\cdot}C_3H_5}\\ \mathrm{S{-}CS}\end{array},$$

forms spherical aggregates of orange needles and melts at 146°.

3-*Phenyl*-5-o-*hydroxybenzylidenerhodanic acid*,

$$\mathrm{OH{\cdot}C_6H_4{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO{\cdot}NPh}\\ \mathrm{S{-}CS}\end{array},$$

from salicylaldehyde, crystallises in chrome-yellow needles, melts at 172°, and dissolves in alkalis to red solutions. The *acetyl* derivative crystallises from alcohol in white needles and melts at 202°.

3-*Methylrhodanic acid*, $\mathrm{CH_2}<\begin{array}{l}\mathrm{CO{\cdot}NMe}\\ \mathrm{S{-}CS}\end{array}$, prepared by heating a solution of methylthiocarbimide and thioglycollic acid in dilute alcohol, crystallises from water in slender, white needles and melts at 72°.

It is neutral and is isomeric with the 5-methylrhodanic acid prepared by Berlinerblau (Abstr., 1886, 326).

5-*Benzylidene-3-methylrhodanic acid*, from benzaldehyde and 3-methylrhodanic acid, crystallises from alcohol in woolly, sulphur-yellow needles and melts at 169°.

5-p-*Methoxybenzylidene-3-methylrhodanic acid*,

$$OMe\cdot C_6H_4\cdot CH{:}C{<}\begin{matrix}CO\cdot NMe\\ S-CS\end{matrix},$$

from anisaldehyde, forms felted, golden-yellow needles and melts at 181°.

5-m-*Nitrobenzylidene-3-methylrhodanic acid* forms greenish-yellow needles and melts at 233°.

5-p-*Nitrobenzylidene-3-methylrhodanic acid* forms orange scales and melts at 205°.

5-p-*Hydroxy*-m-*methoxybenzylidene-3-methylrhodanic acid*, from vanillin and 3-methylrhodanic acid, forms orange needles and melts at 199°.

5-*Methylenedioxybenzylidene-3-methylrhodanic acid*,

$$CH_2{:}O_2{:}C_6H_3\cdot CH{:}C{<}\begin{matrix}CO\cdot NMe\\ S-CS\end{matrix},$$

from piperonal, forms microscopic, yellow needles and melts at 204°.

5-*Cinnamylidene-3-methylrhodanic acid*,

$$CHPh{:}CH\cdot CH{:}C{<}\begin{matrix}CO\cdot NMe\\ S-CS\end{matrix},$$

forms dark orange-coloured needles and melts at 226°.

3-*Ethylrhodanic acid*, $CH_2{<}\begin{matrix}CO\cdot NEt\\ S-CS\end{matrix}$, prepared from thioglycollic acid and ethylthiocarbimide, is an uncrystallisable oil, but yields highly-crystalline condensation products.

5-*Benzylidene-3-ethylrhodanic acid* crystallises from 70 per cent. alcohol in flat, glistening, greenish-yellow needles and melts at 149°.

5-o-*Hydroxybenzylidene-3-ethylrhodanic acid* forms orange needles with blue reflex and melts at 190°.

5-p-*Methoxybenzylidene-3-ethylrhodanic acid*, forms felted, yellow needles and melts at 143°.

5-m-*Nitrobenzylidene-3-ethylrhodanic acid* forms glistening, greenish-yellow leaflets or flat needles and melts at 188°.

5-p-*Hydroxy*-m-*methoxybenzylidene-3-ethylrhodanic acid* forms felted, yellow needles and melts at 140°.

5-*Methylenedioxybenzylidene-3-ethylrhodanic acid* forms woolly, yellow needles and melts at 154°.

5-*Cinnamylidene-3-ethylrhodanic acid* forms yellow scales and melts at 187°.

3-*Phenyl-5-methylrhodanic acid*, $CHMe{<}\begin{matrix}CO\cdot NPh\\ S-CS\end{matrix}$, prepared by boiling phenylthiocarbimide and α-thiolactic acid in dilute alcohol or by boiling an alcoholic solution of ammonium phenyldithiocarbamate and ethyl α-bromopropionate, crystallises from alcohol in thin, greenish-white plates, melts at 118—119°, and does not form condensation products with aldehydes. C. H. D.

Methods for obtaining Organic Bases from Vegetable Juices and Extracts. ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1904, **59**, 344—354. Compare Abstr., 1895, ii, 364).—The following method is employed for the isolation of hexone bases. The extract, after precipitation with lead acetate, or tannic acid and lead acetate, is treated with phosphotungstic acid, and the precipitate rubbed with an excess of pure barium hydroxide and cold water. If any odour of ammonia is noticed, the ammonia is removed by passing air through the cold liquid. The filtered solution is then treated with carbon dioxide, exactly neutralised with nitric acid, and evaporated to a small volume, a little nitric acid being added from time to time to maintain neutrality. It is then precipitated with silver nitrate and filtered. More silver nitrate is added to the filtrate, until a drop of the solution gives a brownish-yellow precipitate with baryta water. Then the histidine and argenine are successively precipitated (as silver compounds) by baryta (Kossel and Kutscher, *Zeit. physiol. Chem.*, **31**, 170—175). The argenine-silver precipitate is purified by Kossel's method. The histidine precipitate is treated with dilute hydrochloric acid, filtered, and precipitated with phosphotungstic acid. The precipitate is decomposed with baryta, the filtrate treated with carbon dioxide, and the histidine precipitated with mercuric chloride. The product is finally treated with hydrogen sulphide. The precipitation with mercuric chloride is not complete, and involves loss of substance, but the method yields a pure product.

The filtrate from the arginine silver compound is neutralised with hydrochloric acid and evaporated down. After removing the inorganic salts as far as possible, the residue is extracted with hot absolute alcohol, which dissolves the hydrochlorides of choline, betaine, trigonelline, stachydrine, and guanidine, leaving a residue which may contain lysine. The further separation of the bases is effected by means of the mercurichlorides and platinichlorides. N. H. J. M.

Mutual Solubility of Nicotine and Water. C. S. HUDSON (*Zeit. physikal. Chem.*, 1904, **47**, 113—115).—Nicotine and water are miscible in all proportions at temperatures below 60° and above 210°. At temperatures between 60° and 210°, the miscibility is limited, except when one of the components is in very large excess. Above 90°, a saturated solution of water in nicotine is lighter than a saturated solution of nicotine in water; below 90°, the reverse is the case. When nicotine is mixed with water, much heat is developed, probably owing to the formation of a hydrate. The marked variation of the rotation and of the refraction with the concentration points to the same interpretation. To the presence of such a hydrate the miscibility of the two otherwise immiscible liquids, nicotine and water, may be attributed. J. C. P.

Action of Bromine on Strychnine. LÉON MARTIN (*Bull. Soc. Chim.*, 1904, iii, **31**, 386—391).—*Bromostrychnine*, $C_{21}H_{21}O_2N_2Br$, prepared by the addition of bromine dissolved in hydrobromic acid (50 per cent.) to an aqueous solution of strychnine hydrobromide in presence of hydrobromic acid and sodium acetate until the orange

yellow precipitate formed on each addition of the reagent begins to be permanent, crystallises from warm alcohol on diluting with water in colourless needles and melts at 199°. The *methiodide* forms slightly yellow needles and melts at 298°; the *ethiodide* melts at 272°.

When the liquid in which bromostrychnine has been produced is poured into excess of the brominating mixture, *bromostrychnine bromide hydrobromide*, $C_{21}H_{21}O_2N_2Br,Br,HBr$, is formed; this is a crystalline, yellow powder, which melts at 204° and dissolves in neutral solvents with the liberation of one atom of bromine; the latter is also removed by sodium thiosulphate. The substance becomes resinous on exposure to light.

Dibromostrychnine, produced by brominating bromostrychnine at 100°, forms small crystals, which become coloured on exposure to light; it melts at 130—131° and is soluble in alcohol. The *methiodide* melts at 243° and the *ethiodide* at 251°.

Dibromostrychnine bromide hydrobromide, prepared from the foregoing, like the analogous monobromo-compound forms microscopic, yellow crystals and melts at 146°. On exposure to light or heat it becomes resinous.

Iodostrychnine iodide hydriodide, prepared by the addition of hydrobromic acid to a boiling solution of strychnine in dilute iodic and sulphuric acids, is a brown substance which melts at 154°, and when treated with acetone and subsequently with ammonia solution furnishes *iodostrychnine*; this is a maroon-coloured, crystalline powder which melts at 188°.

Strychnine di-iodide, $C_{21}H_{22}O_2N_2,I_2$, obtained by the action of iodine (2 atoms) on the alkaloid (1 mol.) in the presence of sodium acetate and hydriodic acid, forms ruby-red crystals, dissolves partially in organic solvents with the liberation of iodine, and melts with decomposition. T. A. H.

Transformations of the Nitrosopyrroles. Francesco Angelico and Enrico Calvello (*Gazzetta*, 1904, 34, i, 38—50. Compare this vol., i, 188).—*Sodium* 3-iso*nitroso*-2 : 4-*dimethylpyrrole*,

$$N\Big\langle\begin{matrix}CMe\cdot C{:}N\cdot ONa\\ |\\ CH{-}CMe\end{matrix},$$

prepared by the action of amyl nitrite on an alcoholic solution of pyrrole containing sodium ethoxide, forms reddish-yellow crystals; when it is decomposed by dilute sulphuric acid, and extracted with ether, a beautiful, transitory green colour is imparted to the solvent, showing the formation of the true nitroso-compound, $NH\Big\langle\begin{matrix}CMe{:}C\cdot NO\\ CH{=}CMe\end{matrix}$.

Sodium 3-iso*nitroso*-2 : 5-*dimethylpyrrole* was also prepared; it is decomposed by a cold alkaline solution of hydroxylamine giving the *trioxime*, $OH\cdot N{:}CMe\cdot C(N\cdot OH)\cdot CH_2\cdot CMe{:}N\cdot OH$, of a *hexane-βγε-trione*, which separates from alcohol in magnificent white crystals, melts at 159°, and gives a *tribenzoyl* derivative, $C_{27}H_{23}O_6N_3$, decomposing at 180°. On warming the trioxime with dilute sulphuric acid, a *substance*, $C_6H_8O_2N_2$, is obtained by the loss of hydroxylamine,

crystallising from light petroleum in needles and melting at 117°; several formulæ may be given to the substance. That it contains a hydroxyl group is shown by its giving a *benzoyl* derivative,

$C_{13}H_{12}O_3N_2$,

which crystallises from benzene in minute needles and melts at 180—181°; with phenylcarbimide, the compound $C_{13}H_{13}O_3N_3$ is formed, melting at 178—180°. The final action of sulphuric acid on the trioxime is to form a *substance* $C_6H_7O_2N$, probably $CH \lessdot \begin{matrix} CMe{\cdot}O \\ CAc{:}N \end{matrix}$ or $CH \lessdot \begin{matrix} CMe{:}N \\ CAc{-}O \end{matrix}$, which crystallises in nacreous leaflets, melts at 22°, boils at 177°, and with iodine and aqueous potassium hydroxide gives rise to iodoform; the p-*nitrophenylhydrazone*, $C_{12}H_{12}O_3N_4$, crystallises from alcohol in lustrous, yellow needles and melts and decomposes at 235°. W. A. D.

Dinitrophenylpyridinium Chloride and its Products of Change. Theodor Zincke (*Annalen*, 1904, **330**, 361—374).—1-Chloro-2 : 4-dinitrobenzene reacts with pyridine giving the chloride of the ammonium base, $C_5H_5NCl{\cdot}C_6H_3(NO_2)_2$, which reacts with alkali hydroxides in the following manner: if the aqueous solution is made alkaline, a brownish-red precipitate separates and a violet solution is formed; on now adding acid to the whole, a brilliant red precipitate is formed. This material is also produced when an alkali hydroxide is added drop by drop to the acid solution, the solution never becoming permanently alkaline. This substance appears possibly to be the *pseudo-base*, $CH \lessdot \begin{matrix} CH{=\!=\!=}CH \\ CH{\cdot}CH(OH) \end{matrix} \gtrdot N{\cdot}C_6H_3(NO_2)_2$, as it dissolves in alkali hydroxides and is changed, although but slowly, back into the ammonium base (compare Spiegel, Abstr., 1900, i, 51; 1901, i, 752; Vongerichten, Abstr., 1900, i, 51; Reitzenstein, Abstr., 1903, i, 815). The red substance is nearly quantitatively converted into the ammonium base, when it is heated with an acetic acid solution of hydrogen chloride, but when the red compound is treated with aqueous hydrochloric acid, 2 : 4-dinitroaniline is formed, a fact which favours the view that the red substance is represented by the formula $C_6H_3(NO_2)_2{\cdot}N{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CHO$; all attempts to isolate the corresponding dialdehyde together with the dinitroaniline in the action of hydrochloric acid failed. It has, however, been obtained in the form of a dianilide, $NPh{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}NHPh$, when the red substance or the tertiary ammonium salt is allowed to interact with aniline; from the ammonium salt, dinitroaniline is formed at the same time; the free *base* crystallises in orange-yellow leaflets and the *hydrochloride* in red needles. When boiled with hydrochloric acid or heated for a short time at its melting point, the hydrochloride of the dianilide is decomposed into aniline and *phenylpyridinium chloride*, the pyridine ring being again regenerated. This tertiary ammonium salt can be directly prepared from the dinitrophenylpyridinium chloride by heating it with aniline at 100° for a considerable time.

When the dianilide is treated with excess of bromine, it is con-

verted into *s*-tribromoaniline and the *perbromide* of *s*-tribromophenylpyridinium bromide, $C_5H_5NBr_3 \cdot C_6H_2Br_3$, which is not affected by aniline.

Both the dinitroammonium salt and the red substance obtained from it by the action of alkalis are converted by phenylhydrazine, even in the cold, into the *anilino-phenylhydrazide*,

$$C_6H_3(NO_2)_2 \cdot N \colon CH \cdot CH \colon CH \cdot CH \colon CH \cdot N_2H_2Ph,$$

which crystallises in lustrous, black needles.

It is noteworthy that the dianilide and anilino-phenylhydrazide are intensely coloured, a property which appears to depend on the unsaturated carbon chain, since Claisen (this vol., i, 14) found that the dianilide of propargylaldehyde is coloured. K. J. P. O.

A New Class of Colouring Matters derived from Pyridine. W. König (*J. pr. Chem.*, 1904, [ii], 69, 105—137).—When pyridine is mixed with cyanogen bromide in ethereal solution, and a primary aromatic amine is then added, it seems that the pyridine and cyanogen bromide first form an additive product, which then reacts with the amine quantitatively according to the equation

$$CH \lessdot \begin{matrix} CH \colon CH \\ CH \cdot CH \end{matrix} \gtrdot NBr \cdot CN + NH_2R =$$

$$CH \lessdot \begin{matrix} CH \cdot CH(NHR) \\ CH \!=\!=\!=\!=\!=\!= CH \end{matrix} \gtrdot NHRBr + CN \cdot NH_2 ;$$

cyanamide remains in solution, whilst the *arylaminoaryldihydropyridinium bromide* is precipitated. This has a colour varying from red to blue, and crystallises well from acetic acid, alcohol, &c.; it dyes fabrics of animal origin, and also vegetable fabrics to some extent, but the dyed fabrics will not bear washing. When the colouring matter is heated with concentrated hydrochloric acid at 160° for several hours, it is hydrolysed to the amine, NH_2R, and an *arylpyridinium* chloride, $CH \lessdot \begin{matrix} CH \colon CH \\ CH \cdot CH \end{matrix} \gtrdot NRCl$. The corresponding base separates in an impure state when the solution is made alkaline; it is best purified by dissolving it in hydrochloric acid and adding the solution to a concentrated solution of ferric chloride, when a compound with $1FeCl_3$ separates, which can be purified by crystallisation from acetic acid. From the solution of this compound, the iron can be precipitated with sodium hydroxide, and other salts may be prepared from the remaining solution by the addition of suitable acids. The phenyl colouring matter ($R = Ph$) yields aniline and a little pyridine when distilled; bromine does not simply brominate it, but decomposes it into tribromoaniline and phenylpyridinium bromide.

The colouring matters may also be prepared from a solution of pyridine and the amine in an acid, and instead of pure cyanogen bromide the aqueous solution of that substance obtained in its preparation may be used; it is usually necessary to add an alkali in order to get the colouring matter formed. In the case of an amino-acid, the sodium salt may be used suitably. The pure base can be precipitated with alcoholic ammonia from the solution of its chloride in alcohol, and from it, salts with other acids can be prepared. Some of these colouring matters crystallise from different solvents in forms

which appear quite different; these may perhaps be examples of stereoisomeric derivatives of quinquevalent nitrogen. That one of the residues in the amine enters the 2 or 6 position in the pyridine ring is apparent from the fact that 2-methylpyridine (picoline) yields a colouring matter, but 2 : 4 : 6-trimethylpyridine (collidine) does not. In one case (methylaniline), a colouring matter was obtained from a secondary amine, which was soluble in hot water, although not in cold. The formation of a colouring matter from pyridine, a primary amine, and cyanogen bromide may be used as a test for either of these substances. The following substances were prepared and analysed; the temperatures are melting points.

Arylaminoaryldihydropyridinium Bromides.—From aniline, $R = Ph$, 162°; *m*-xylidine, $R = C_6H_3Me_2$, 153°; ψ-cumidine, $R = 1:3:4\text{-}C_6H_2Me_3$, 158°; the naphthylamines, $R = C_{10}H_7$; β, 182°; α, 158°; *p*-phenetidine, $R = C_6H_4{\cdot}OEt$, 143°; *p*-aminophenol, $R = C_6H_4{\cdot}OH$, 181°; sodium sulphanilate, $R = C_6H_4{\cdot}SO_3Na$ and $(NH){<}\frac{C_6H_4}{O}{>}SO_2$; aminoazobenzene, $R = C_6H_4{\cdot}N{:}NPh$, 159°; methylaniline, $NHR = NMePh$, 139°. From 2-methylpyridine (picoline) and *o*-toluidine, 143°.

Arylpyridinium Salts.—From aniline, $R = Ph$; *ferrichloride*, 158°; *platinichloride*, 206° (decomposes); *aurichloride*, 182°; *dichromate*, 123°; *ferrichloride* of the *bromide*, 123°. From the naphthylamines: β: *ferrichloride*, 130°; *platinichloride*, 194° (with decomposition); *aurichloride*, 203°; *iodide*, 201°; α: *ferrichloride*, 119—120°; *picrate*, 192—193°. C. F. B.

Preparation of Indole from Indoxyl. DANIEL VORLÄNDER and O. APELT (*Ber.*, 1904, 37, 1134—1135).—A good yield of indole is obtained by reducing indoxyl or indoxylic acid in alkaline solution with sodium amalgam or zinc dust. The best material is the product obtained by fusing indoxylic acid with sodium hydroxide. The mixture is distilled with steam, when a part of the indoxyl condenses in crystalline form, and the remainder may be precipitated as the picrate.

1-Methylindole is obtained in similar manner from 1-methylindoxylic acid. C. H. D.

Ammonium Compounds. Methylation of 5-Phenylacridine-*o*-carboxylic Acid. HERMAN DECKER and THEODOR HOCK (*Ber.*, 1904, 37, 1002—1012. Compare Abstr., 1903, i, 518).—When 5-phenylacridine-*o*-carboxylic acid, $C_6H_4{<}\frac{C(C_6H_4{\cdot}CO_2H)}{N}{>}C_6H_4$ (Bernthsen, Abstr., 1884, 1356), is heated with methyl iodide for 4 hours at 120°, it gives the *hydriodide* of the methyl ester,

$$C_6H_4{<}\frac{C(C_6H_4{\cdot}CO_2Me)}{N}{>}C_6H_4.$$

The *methyl* ester itself is obtained by substituting the sodium salt for the free acid, or by heating the acid with methyl alcohol containing hydrogen chloride; it crystallises from xylene in bright yellow needles and melts at 173°. The *hydriodide* forms dark-red, fan-shaped aggregates of crystals and melts at 228—230°; the *picrate*,

$C_{27}H_{18}O_9N_4$, melts at 241° and the *dichromate* crystallises with $1H_2O$, and melts when anhydrous at 147°.

On heating the methyl ester with methyl sulphate for 2 hours at 120° and adding potassium iodide, the *methiodide*,

$$C_6H_4 < \begin{matrix} C(C_6H_4 \cdot CO_2Me) \\ NMeI \end{matrix} > C_6H_4,$$

is obtained; it crystallises in garnet coloured needles and melts at 226—227°. The *picrate*, $C_{26}H_{18}O_9N_4$, of the *N*-methyl derivative, melts at 201°; with chromic acid, an abnormal *trichromate*,

$$(C_{22}H_{18}O_2N)_2Cr_2O_7,CrO_3,$$

is obtained, crystallising in small, orange coloured cubes. When any one of these esters is decomposed by cold aqueous sodium hydroxide, the *lactone*,

$$NMe < \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > C < \begin{matrix} O \\ C_6H_4 \end{matrix} > CO,$$

of 5-*hydroxy*-5-*phenyl*-10-*methyldihydroacridinecarboxylic acid* is obtained; it crystallises from benzene or xylene in white leaflets or cubes, melts at 245°, sublimes unchanged, and dissolves in acids giving salts derived from the betaine *compound*,

$$C_6H_4 \left< \begin{array}{l} C - C_6H_4 - CO \\ \;| > C_6H_4 \quad\;\; | \\ NMe ——— O \end{array} \right. .$$

Thus, on dissolving it in hydrochloric acid and adding potassium iodide, the *iodide*, $C_6H_4 < \begin{matrix} C(C_6H_4 \cdot CO_2H) \\ | \\ NMeI \end{matrix} > C_6H_4$, is formed, which crystallises from water with $1H_2O$; the corresponding *picrate*, $C_{27}H_{18}O_9N_4$, crystallises from alcohol in large, lustrous, yellow prisms and melts at 212—215°; the *dichromate* is an orange-red, crystalline powder melting at 252—255°. W. A. D.

Some Amino- and Aminohydroxy-diphenylamines. ROBERT GNEHM [with H. BOTS] (*J. pr. Chem.*, 1904, [ii], 69, 161—175).—A detailed description is given of the preparation of *p*-dimethylamino-*p*-hydroxydiphenylamine and some of its derivatives (compare Abstr., 1902, i, 831). When the base is heated for 24 hours at 110° with a solution of sulphur in concentrated aqueous sodium sulphide, the leuco-derivative of a blue *colouring matter*, $C_{14}H_{12}O_2N_2S_3$, is formed; it can be oxidised to the latter by aspirating air through its alkaline solution. The colouring matter is soluble in alkali hydroxides and in concentrated, although not in dilute, acids; an amorphous *zinc* salt, $C_{14}H_{10}O_2N_2S_3Zn$, a crystalline *sodium hydrogen sulphite* compound, $C_{14}H_{12}O_2N_2S_3,NaHSO_3,2H_2O$, and an amorphous *diacetyl* derivative were prepared and analysed.

When a solution of *p*-aminophenol and *o*-toluidine in dilute sulphuric acid is oxidised with sodium dichromate, a *colouring matter* is formed; addition of sodium sulphide then effects a reduction to the leuco-derivative, p-*aminotolyl*-p-*hydroxyphenylamine*,

$$NH_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4 \cdot OH,$$

which can be crystallised from water; it melts at 159—160°.

A blue *colouring matter* is formed when molecular proportions of dimethyl-*p*-phenylenediaminethiosulphonic acid and phenol, dissolved

in dilute aqueous sodium carbonate, are oxidised at 0° with 2 per cent. aqueous sodium hypochlorite; the sodium salt can be salted out with sodium chloride, and can be reduced to the leuco-derivative by means of hydrogen sulphide, but neither substance was obtained pure.

C. F. B.

Methyldiaminodiarylmethane-ω-sulphonic Acids. ANILINFARBEN- & EXTRACT-FABRIKEN VORM JOH. RUD. GEIGY (D.R.-P. 148760).—Aromatic amino-compounds in which either an ortho- or a para-position is unoccupied react with formaldehyde and sulphurous acid, slowly at the ordinary temperature, rapidly at 70—90°, forming methyldiaminodiarylmethane-ω-sulphonic acids, which are diazotisable, and are readily hydrolysed to diaminodiarylmethane, formaldehyde, and alkali sulphite.

Methyl-4 : 4′-*diaminodiphenylmethane-ω-sulphonic acid*,

$$NH_2·C_6H_4·CH_2·C_6H_4·NH·CH_2·SO_3H,$$

from aniline, formaldehyde, and sulphurous acid, is a white powder, melting and decomposing at 168°. The *ammonium* salt forms silvery needles and dissolves readily in water. 3 : 3′-*Dichloromethyl*-4 : 4′-*diaminodiphenylmethane-ω-sulphonic acid*, from *o*-chloroaniline, melts at 168—169°. *Methyl*-4 : 4′-*diamino*-3 : 3′-*ditolylmethane-ω-sulphonic acid*, from *o*-toluidine, is an almost insoluble powder, melting at 172°. *Methyl*-4 : 4′-*diamino*-2 : 2′-*ditolylmethane-ω-sulphonic acid*, from *m*-toluidine, melts at 178—180°. *Methyl*-2 : 2′-*diamino*-3 : 3′-*ditolylmethane-ω-sulphonic acid*, from *p*-toluidine, melts at 159—160°. *Methyl*-4 : 4′-*diaminodixylylmethane-ω-sulphonic acid* melts at 170° and forms a sparingly soluble *ammonium* salt. *Methyldiaminodinaphthylmethane-ω-sulphonic acid*, from α-naphthylamine, is crystalline and melts at 193—195°.

C. H. D.

Action of Phosphorus Pentachloride on Trisubstituted Carbamides. A. STEINDORFF (*Ber.*, 1904, 37, 963—966).—*Triphenylchloroamidine*, prepared by the action of phosphorus pentachloride on triphenylcarbamide at 120°, distils at 240—250° under 24 mm. pressure, and forms colourless crystals, melting at 90—92°. It reacts with aniline, forming *tetraphenylguanidine*, which melts at 137—140°, and yields a *platinichloride* melting at 240—242°; with diphenylamine, it gives *pentaphenylguanidine*, melting at 177—179°.

*Ethyl*iso*triphenylcarbamide*, prepared by the action of sodium and alcohol on the amidine, boils at 210—220° under 35 mm. pressure and melts at 48—50°; its *platinichloride* melts at 81—83°. iso*Tetraphenylthiocarbamide*, prepared by the action of sodium and thiophenol in alcoholic solution on the amidine, melts at 185—188°, is soluble in concentrated acids, and forms a *platinichloride* melting at 135—138°.

Diphenyltolylchloroamidine distils at 240—250° under 30 mm. pressure, and melts at 105—107°; it is prepared and reacts with bases in a similar manner to the triphenylchloroamidine.

E. F. A.

Benzidine Transformation. J. POTTER VAN LOON (*Rec. trav. chim.*, 1904, 23, 62—97. Compare Abstr., 1903, i, 249).—The author has investigated the respective influences of the various factors in the con-

version of hydrazobenzene into benzidine by the action of acids. The amount of benzidine formed at first increases with the concentration of the acid and ultimately decreases with this; it is independent of the nature of the acid, and diminishes (1) as water is replaced by methyl or ethyl alcohol as a solvent and (2) as the temperature is increased. Tables illustrating these statements are given in the original. At 100°, hydrazobenzene is partially decomposed into azobenzene and aniline.

Determinations of the velocity of the transformation into benzidine were made under various conditions. Using 50 per cent. alcohol and normal hydrochloric acid, the value of k was found to be 0·345 to 0·391; with 15 per cent. alcohol and with $N/10$, $N/20$ and $N/40$ hydrochloric acid, the values of k found were respectively 0·213 to 0·238, 0·296 to 0·310, and 0·383 to 0·500. The foregoing determinations were made at 25°; with $N/20$ acid and 15 per cent. alcohol at 30·2°, the value of k was 0·520 to 0·557. The variations in the value of k for *each* concentration of acid are regarded as due to secondary hydrolysis, and the variations in this constant for different concentrations of acid, it is suggested, may be due to the concentration of hydrazobenzene not remaining constant, in spite of precautions taken to ensure this, during the experiments.

The value of k for nitric acid is similar to that found for hydrochloric acid under the same conditions, and that for dichloroacetic acid has about one-fourth this value. These results indicate that the transformation is due solely to the hydrogen ions of the acid. T. A. H.

Conversion of Derivatives of Hydrazine into Heterocyclic Compounds. ROBERT STOLLÉ (*J. pr. Chem.*, 1904, [ii], 69, 145—160. Compare *ibid.*, 68, 130).—A detailed description of experiments that have been described briefly already (Abstr., 1899, i, 413, 456).

Tribenzoylhydrazine, CPhO·NBz·NHBz or OBz·CPh:N·NHBz, appears to be described for the first time. It is obtained from benzoyl chloride and dibenzoylhydrazine in the presence of pyridine, or from benzoyl chloride and sodiodibenzoylhydrazine, or by boiling azodibenzoyl with water or dilute alcohol; it melts at 212°, and decomposes into diphenylfurodiazole and benzoic acid when maintained at 200°.

From benzoyl chloride and dibenzoylhydrazine, in benzene solution in the presence of pyridine, Weindel has obtained a second tribenzoylhydrazine, melting at 198°; the two substances are perhaps the tautomeric modifications. C. F. B.

[Ethyl Phenylsemicarbazide-α carboxylate.] A Correction. SALOMON F. ACREE (*Ber.*, 1904, 37, 995. Compare *ibid.*, 622).—The statement previously made that an ethyl ester was formed by the interaction of silver phenylsemicarbazide-α-carboxylate and ethyl iodide is incorrect; the silver salt used contained a small quantity of the ester as impurity. E. F. A.

Benziminazoles and Dyes derived from them. OTTO KYM (*Ber.*, 1904, 37, 1070—1074).—opp'-*Trinitrotribenzoyl-triaminodiphenylamine*, $C_{33}H_{23}O_9N_7,H_2O$, prepared by the Schotten-Baumann method, crystallises from acetic acid and water in yellowish-green, glistening flakes, melts at 180—190°, becomes solid on further heating, and again

melts at 303—304°; it is very sparingly soluble in all solvents except nitrobenzene, from which it separates in minute, yellow, anhydrous needles.

5-*Amino*-1-p-*aminophenyl*-2-p-*aminophenylbenziminazole*,

$$\begin{array}{l} NH_2\cdot C_6H_3\cdot N\cdot C_6H_4\cdot NH_2 \\ \quad\quad\; N{=\!=}C\cdot C_6H_4\cdot NH_2 \end{array},$$

prepared by energetic reduction of the preceding compound with tin and hydrochloric acid, crystallises from dilute alcohol in minute, greyish-white needles and melts at 223—224°.

p-*Nitro*-o-p′-*diaminodiphenylamine*,

$$NO_2\cdot C_6H_3(NH_2)\cdot NH\cdot C_6H_4\cdot NH_2,$$

prepared by reducing dinitroaminodiphenylamine with sodium sulphide, crystallises from alcohol in long, reddish-black needles with a metallic lustre, and melts at 188—189°.

5-*Nitro*-2-p-*nitrophenyl*-1-p-*nitrobenzoylaminophenylbenziminazole*,

$$\begin{array}{l} NO_2\cdot C_6H_3\cdot N\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2 \\ \quad\quad\quad N{=\!=}C\cdot C_6H_4\cdot NO_2 \end{array},$$

prepared by heating the preceding compound at 180—200° with *p*-nitrobenzoyl chloride, crystallises from acetic acid in minute, heavy, yellow crystals, melts at 299—300°, and is reduced by tin and hydrochloric acid to the iminazole base just described; the yield of the base is, however, not large.

When diazotised and coupled with naphtholsulphonic acid, the iminazole base does not give deeper shades than the mono- and di-amino-compounds, but, on the contrary, the shade is distinctly redder. Neither do the second and third amino-groups increase the affinity of the diazo-dye for the cotton fibre or the depth of colour that can be produced, and it would therefore appear that the presence of a free (undiazotised) amino-group has little influence on this property. T. M. L.

[Precipitation of Rosaniline Solutions by Alkali.] HUGO WEIL (*Ber.*, 1904, 37, 1014—1015).—A reply to Jennings (*Ber.*, 1903, 36, 4022). W. A. D.

Colour Bases of the Triphenylmethane Dyes. ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1904, 37, 1183—1184. Compare Abstr., 1902, i, 112, 355; 1903, i, 811, this vol., i, 308).—The aniline-blue corresponding with triphenylrosaniline, when acted on by alkali hydroxides, yields not the colourless carbinol, but a black *phenylimide*, $C_{37}H_{29}N_3$, which behaves in a similar manner to the phenylimide of monoaminotriphenylcarbinol (*loc. cit.*). Paramagenta, when powdered with sodium hydroxide, yields quantitatively a polymeride of the *imide*, $C_{19}H_{17}N_3$, crystallising from xylene in almost colourless needles. The authors propose to discuss these observations at a later date.

E. F. A.

Preparation of Formyl-4 : 5-diamino-2 : 6-dihydroxy-1 : 3-dimethylpyrimidine. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D. R.-P. 148208).—Formyl-4 : 5-diamino-2 : 6-dihydroxy-1 : 3-dimethylpyrimidine (Traube, Abstr., 1900, i, 416) may be prepared by methylating the formyl derivatives of 4 : 5-diamino-2 : 6-dihydroxypyrimidine

or 4 : 5-diamino-2 : 6-dihydroxy-3-methylpyrimidine by means of methyl iodide or methyl chloride at 30—40°. The presence of an excess of alkali must be avoided, or theophylline will be formed (Abstr., 1903, i, 527). C. H. D.

Preparation of Azine Compounds. KALLE & Co. (D.R.-P. 148113).—Sodium sulphide reduces the trinitrodiphenylamine,

$$C_6H_3(NO_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

prepared from 1-chloro-2 : 4-dinitrobenzene and *m*-nitroaniline, on warming. The nitro-compound dissolves at first, and an *azine*,

$$NH_2{\cdot}C_6H_3{<}\overset{N}{\underset{N}{|}}{>}C_6H_3{\cdot}NH_2,$$

separates in reddish-bronze needles or leaflets. Alcoholic or ethereal solutions of the azine show an orange fluorescence. Acids form three series of salts, green, red, and blue; reducing agents decolorise these solutions, the leuco-compound dissolves in ether to a fluorescent solution and oxidises in air.

Similar azines are obtained from such trinitro- or polynitro-diphenylamines as contain at least one nitro-group in the *ortho*- and another in the *meta*-position to the imino-group. Thus the trinitrophenyltolylamine prepared from 1-chloro-2 : 4-dinitrobenzene and 2-nitro-4-aminotoluene yields a *eurhodine*, resembling the above compound, but yellower in colour. C. H. D.

Action of Chromic Acid on Diphenylcarbazide. A. MOULIN (*Bull. Soc. chim.*, 1904, [iii], 31, 296—300. Compare Cazeneuve, Abstr., 1901, i, 655).—When diphenylcarbazide, dissolved in a mixture of alcohol (90°) with 10 per cent. of acetic acid, is added to chromic acid dissolved in water, there is formed a violet coloured product, which, after extraction with chloroform, may be obtained in brilliant spangles. It is soluble in alcohol and acetic and sulphuric acids, and has approximately the composition required by the formula

$$C_{41}H_{44}O_{16}N_{10}Cr.$$

When the diphenylcarbazide solution is added to more concentrated solutions of chromic acid, the violet coloration first produced gives place to a reddish-brown colour, and a mixture of hydrogen and nitrogen is evolved. A voluminous brown precipitate eventually separates, which, when washed with alcohol, leaves a maroon-coloured product which is insoluble in the usual solvents and contains 17·8 to 18·3 per cent. of chromium. The portion of the crude brown precipitate soluble in alcohol forms garnet-coloured spangles and is soluble in acetic acid: it contains 1·52 per cent. of chromium.

T. A. H.

Action of Bleaching Powder on Diazo- and *iso*Diazo-compounds. THEODOR ZINCKE and A. KUCHENBECKER (*Annalen*, 1903, 330, 1—37).—I. When bleaching powder is allowed to act on diazobenzenesulphonic acid, two substances are formed. 2 : 2′-*Dinitroazobenzene*-4 : 4′-*disulphonic acid*, $N_2\left[C{<}{\begin{matrix}C(NO_2){:}CH\\CH{-\!-\!-}CH\end{matrix}}{>}C{\cdot}SO_3H\right]_2$, is obtained by adding a mixture of sodium sulphanilate and sodium

nitrite in aqueous solution to ice-cold sulphuric acid, and then pouring into the whole a solution of bleaching powder containing 4 per cent. of hypochlorous acid; the calcium salt slowly separates; the free acid prepared from the silver salt crystallises in slender, reddish-yellow needles; the *sodium*, *silver*, and barium salts (each with $2H_2O$) are described. 4 : 6-Dichloro-2-nitroaniline (m. p. 100°), which is also produced, is contained in the alcoholic washings of the calcium salt above mentioned.

It is suggested that the initial product of the action of bleaching powder on diazobenzenesulphonic acid is a diazonium hypochlorite, which is then converted into a nitroamine; in the presence of acid, the latter changes into the isomeric nitrosulphanilic acid, which is oxidised by the bleaching powder to the azo-compound. The dichloronitroaniline is produced by chlorination of the nitrosulphanilic acid, when the sulphonic acid group is displaced by chlorine. By adding salt or concentrated calcium chloride to the solution containing the diazonium salt and the bleaching powder, a white solid separates, which is soluble in water and bleaches; it is possibly the impure diazonium hypochlorite.

2 : 2′-*Diaminoazobenzene*-4 : 4′-*disulphonic acid*, prepared by reducing the sodium salt of the dinitro-compound with 4 per cent. sodium amalgam, crystallises in pale brown needles with $2H_2O$; the alkali salts are very soluble in water, forming blood-red solutions; the *silver* salt crystallises in red, insoluble needles. The base can be diazotised in alcoholic solution by amyl nitrite, the diazo compound,

$$N_2\left(C_6H_3{<}{}^{N_2}_{SO_2}{>}O\right)_2,2H_2O,$$

being a yellow, insoluble powder, which does not dissolve in acids but in alkalis; it couples with β-naphthol. Azobenzene-4 : 4′-disulphonic acid is obtained as a by-product in the reduction of dinitroazobenzene-4 : 4′-disulphonic acid, and was isolated in the form of the sodium salt (Limpricht, Abstr., 1882, 1197).

On reducing the sodium salt of the dinitrosulphonic acid with zinc dust and water at 100° in the presence of ammonium chloride, o-*diaminohydrazobenzene*-4 : 4′-*disulphonic acid*,

$$N_2H_2\left[C{<}{}^{C(NH_2):CH}_{CH\text{———}CH}{>}C\cdot SO_3H\right]_2,$$

is formed; its *sodium* salt is a colourless powder readily oxidising in the air. When the dinitroazo-compound is reduced by tin and hydrochloric acid, *o*-phenylenediamine-*p*-sulphonic acid is formed (Nietzki and Lerch, Abstr., 1889, 144).

II. *Action of Bleaching Powder on Bromo-derivatives of Diazobenzene*-3 : 3′-*disulphonic Acid*.—When a solution of bleaching powder is added to a suspension of diazotised dibromo-*m*-sulphanilic acid in ice-cold water, a red solution is formed, and the calcium salt of *tetrabromoazobenzene*-3 : 3′-*disulphonic acid*, $N_2\left[C{<}{}^{CH:C(SO_3H)}_{CBr\text{———}CH}{>}CBr\right]_2$, separates. The *sodium* salt, with $4H_2O$, forms a carmine-red, crystalline powder.

From *s*-tribromo-*m*-sulphanilic acid under a similar treatment, a very unstable substance is formed, which decomposes in alcoholic

solution, *3-chloro-2 : 4 : 6-tribromo-1-nitrobenzene* being produced; it crystallises in yellow needles melting at 149—150°.

III. *Action of Bleaching Powder on Diazo-compounds not containing a Sulpho group.*—On adding a solution of bleaching powder to an ice-cold solution of benzenediazonium chloride, the liquid became milky, and a thick oil collected, which began immediately to decompose with the evolution of nitrogen; from the products of decomposition, 4 : 6-dichloro-2-nitroaniline was isolated by distilling with steam. From *p*-nitroaniline, a similar unstable oil was obtained, which yielded, with evolution of nitrogen, *p*-dinitroazobenzene (m. p. 216°).

IV. *Action of Bleaching Powder on isoDiazo compounds.*—On treating an aqueous solution of the sodium *iso*diazoxide, derived from *p*-sulphanilic acid, with bleaching powder, the calcium salt of *p-nitroaminobenzenesulphonic acid*, $NO_2\cdot NH\cdot C_6H_4\cdot SO_3H$, separates; this substance was obtained and purified in the form of its normal *sodium* salt, $NO_2\cdot NH\cdot C_6H_4\cdot SO_3Na,H_2O$, which forms colourless crystals, decomposing in boiling water and converted by bleaching powder into the calcium salt of 2 : 2′-dinitroazobenzene-4 : 4′-disulphonic acid. The basic *sodium*, basic *silver*, basic *barium*, and normal *barium* salts are described. The *potassium* salt of the *N*-methyl ester,

$$NO_2\cdot NMe\cdot C_6H_4\cdot SO_3K,$$

is prepared by heating the basic potassium salt with methyl iodide in methyl alcoholic solution, and forms colourless crystals. Some of the salts just mentioned were obtained by Bamberger's method by oxidising the *iso*diazoxide with permanganate. On reducing the nitroamine with sodium nitrite, the diazonium salt of benzene-*p*-sulphanilic acid was obtained; on reduction with tin and hydrochloric acid, *p*-sulphanilic acid was formed; with sodium amalgam, the hydrazine was produced.

The sodium salt of *p*-nitro*iso*diazobenzene was converted by bleaching powder into *p*-nitronitroaminobenzene (m. p. 110°). K. J. P. O.

Action of Bleaching Powder on *o*-Dibromodiazobenzene-*p*-sulphonic Acid. WILHELM LENZ (*Annalen*, 1903, 330, 37—46. Compare preceding abstract).—In the action of bleaching powder on dibromobenzene-*p*-sulphonic acid, an intermediate product, a hypochlorite, can be isolated. 2 : 2′ : 6 : 6′-*Tetrabromoazobenzene*-4 : 4′-*sulphonic acid*, $N_2\left[C\lessgtr\begin{matrix}CBr:CH\\CBr\cdot CH\end{matrix}\gtrless C\cdot SO_3H\right]_2$, is prepared by diazotising sodium dibromosulphanilate with sodium nitrite and sulphuric acid, and adding a solution of bleaching powder to the neutral suspension of the diazo-compound in water, when the calcium salt separates out. The *sodium* salt crystallises in dark red, lustrous needles with $2H_2O$. The *calcium* salt of the intermediate product,

$$\left[N(OH)_2\cdot N(OCl)\cdot C\lessgtr\begin{matrix}CBr:CH\\CBr\cdot CH\end{matrix}\gtrless C\cdot SO_3\right]_2Ca,$$

is obtained by adding to a solution of the sodium dibromosulphanilate a solution of bleaching powder containing excess of calcium chloride; colourless needles separate, which soon become red and have an odour of hypochlorous acid; in aqueous solution, tetrabromobenzeneazo-

4 : 4′-disulphonic acid is formed; treatment with hydrochloric acid sets free chlorine. The *sodium* salt of this substance is prepared from *o*-dibromodiazobenzene-*p*-sulphonic acid by treatment with a solution of bleaching powder containing salt; it is very soluble in water, and has all the characters of the calcium salt.

2 : 6-*Dibromo*-1-*nitroaminobenzene*-4-*sulphonic acid*,

$$NO_2\cdot NH\cdot C{<}{\substack{CBr{:}CH\\ CBr\cdot CH}}{>}C\cdot(SO_3H),$$

is obtained by treating the calcium salt of the intermediate product with dilute hydrochloric acid; the alcoholic solution of the solid product of the reaction deposits the normal calcium salt in soluble, colourless crystals. The basic *barium* (with $2\frac{1}{2}H_2O$), normal *sodium* (with H_2O), and basic *sodium* salts are described. On heating the calcium salt of the nitroamino-sulphonic acid with hydrochloric acid, the sulphonic acid group is displaced by the nitro-group, and 2 : 6-dibromo-4-nitroaniline (m. p. 204°) is formed. K. J. P. O.

Action of Bleaching Powder on Diazotised *m*-Xylidinesulphonic Acid. ANTON MAUÉ (*Annalen*, 1903, 330, 46—49. Compare preceding abstracts).—On adding bleaching powder solution to the diazo-compound obtained from *m*-xylidinesulphonic acid, the calcium salt of *azo*-m-*xylene*-5 : 5′-*disulphonic acid* is obtained. The acid, $N_2\left[C{<}{\substack{CMe\!=\!=\!CH\\ CH\cdot C(SO_3H)}}{>}CMe\right]_2,5H_2O$, crystallises in reddish-yellow plates, which are very soluble in water (compare Jacobsen and Ledderboge, Abstr., 1883, 593); the *silver* salt crystallises in reddish-yellow needles; the *sodium* (with H_2O), basic *calcium* (with H_2O), normal *calcium* (with $3H_2O$), basic *barium* (with $\frac{1}{2}H_2O$), and normal barium (with $2H_2O$) salts are described. K. J. P. O.

Action of Hydrogen Chloride and Hydrogen Bromide on Azobenzenedisulphonic Acids. THEODOR ZINCKE and A. KUCHENBECKER (*Annalen*, 1903, 330, 50—60. Compare preceding abstracts).—A study of the action of hydrogen chloride and bromide on various azobenzenedisulphonic acids has shown that chlorination or bromination takes place, the sulphonic acid group being replaced; the azo-compound is often decomposed, and when methyl groups are present, as in xylene derivatives, diphenylamines are produced.

When the sodium salt of *o*-dinitroazobenzene-*p*-disulphonic acid is heated with concentrated hydrochloric acid under pressure at 160° for three hours, a small quantity of 3 : 4 : 3′ : 4′-tetrachloroazobenzene, $N_2\left(C{<}{\substack{CH{:}CH\\ CCl\cdot CH}}{>}CCl\right)_2$, is produced; it crystallises in slender, flesh-coloured needles melting at 161—162°, and is reduced to 2 : 4-dichloroaniline. With hydrobromic acid, only a very small quantity of the tetrabromoazobenzene is formed; it crystallises in red needles melting at 179°; the main product of the reaction is 1 : 2 : 4 : 6-tetrabromobenzene (m. p. 98°).

4 : 6 : 4′ : 6′-Tetrabromoazobenzene-3 : 3′-disulphonic acid is converted by hydrochloric acid into 2 : 4-*dichloro*-m-*sulphanilic acid*, which forms

small, colourless crystals; at the same time, a small quantity of 2 : 3 : 4-trichloroaniline (m. p. 68°) is produced. Under similar conditions, hydrobromic acid effects analogous decomposition, dibromo-*m*-sulphanilic acid being formed; but instead of a tribromoaniline, 2 : 3 : 4 : 6-tetrabromoaniline (m. p. 115°) is produced.

On heating the sodium salt of *m*-azo-xylenesulphonic acid with hydrochloric acid, o-*aminodixylylaminedisulphonic acid*,

$$CH{<}{\begin{matrix}CMe{-}C(NH_2)\\CMe{:}C(SO_3H)\end{matrix}}{>}C{\cdot}NH{\cdot}C{<}{\begin{matrix}CMe{-\!-\!-}CH\\CH{:}C(SO_3H)\end{matrix}}{>}CMe,H_2O,$$

is formed, and crystallises in yellow needles, which yield colourless alkaline solutions. K. J. P. O.

[Azo-compounds from Acyl-*p*-aminophenols.] Dahl & Co. (D.R.-P. 147530. Compare this vol., i, 207).—Azo-compounds are obtained by combining diazonium compounds with substituted acyl-*p*-aminophenols, in which an *ortho*-position to the hydroxyl is unoccupied. *Acetyl*-4-*aminophenol*-2-*sulphonic acid*, prepared by the action of acetic anhydride on an aqueous suspension of 4-aminophenol-2-sulphonic acid, forms white, soluble needles and melts and decomposes at a high temperature. *Acetyl*-4-*amino*-2-*chlorophenol*, prepared by boiling 2-chloro-4-aminophenol with glacial acetic acid, forms sparingly soluble, white needles and melts at 144°. *Acetyl*-5-*amino*-2-*cresol* forms white needles and melts at 179°. C. H. D.

Azo-compounds from Naphthylaminesulphonic Acids. Badische Anilin- & Soda-Fabrik (D.R.-P. 148881 and 148882. Compare this vol., i, 207).—Azo-dyes may be prepared by diazotising 1-chloro-β-naphthylamine-5-sulphonic acid or β-naphthylamine-1 : 5-disulphonic acid and combining with resorcinol, 2 : 7-dihydroxynaphthalene, or 8-amino-α-naphthol-4-sulphonic acid. The products are very soluble in water or alkalis, but may be precipitated by acids.

1-Chloro-β-naphthylamine-5- or -7-sulphonic acids, or β-naphthylamine-1 : 6- or -1 : 7-disulphonic acids may also be diazotised and combined with β-naphthol. Red diazo-compounds having the formula $OH{\cdot}C_{10}H_5(SO_3Na)N{:}N{\cdot}SO_3Na$ appear to be formed in the case of naphthylaminedisulphonic acid, owing to the action of the sodium sulphite, resulting from the elimination of one sulpho-group, on the hydroxy-diazo-compound. C. H. D.

Disazo-compounds from 2 : 6-Diaminophenol-4-sulphonic Acid. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 148212).—2 : 6-Diaminophenol-4-sulphonic acid may be prepared by reducing 2 : 6-dinitrophenol-4-sulphonic acid with zinc dust and hydrochloric acid, adding sodium acetate, and precipitating with sodium chloride. It crystallises in white spangles, which become dark in air. Disazo-compounds of the type $R{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}N_2{\cdot}R'$ may be prepared by adding one component to the acetic acid solution of the deep yellow tetrazo-compound, and, when the formation of the monoazo-derivative is complete, introducing the solution of the second component in alkali carbonate or hydroxide. C. H. D.

Isomerism of the Diazoxides. Arthur Hantzsch (*Ber.*, 1904, 37, 1084—1087).—The conclusion of Zawidzki (Abstr., 1903, i, 801), that an amphoteric electrolyte which has exceedingly feeble acid properties may nevertheless yield neutral salts with bases has been welcomed by Bamberger (this vol., i, 201) as affording a possible explanation of the isomerism of the diazoxides, and has enabled him to suggest that the diazonium salts and the normal diazoxides may be regarded as derived from a common parent substance (the diazonium hydroxide), if the latter be regarded as an amphoteric electrolyte. As, however, Zawidzki's conclusions are not only in contradiction with the generally-accepted laws of electrochemistry, but have been shown to be based on incomplete evidence (this vol., i, 381), this view can no longer be justified. T. M. L.

Azo-compounds containing a ψ-Aziminobenzene Residue. Kalle & Co. (D.R.-P. 148011).—Disazo-compounds prepared from diazotised *o*-nitroaniline or its derivatives and sulphonic acids of 8-amino-α-naphthol are reduced by sodium sulphide at low temperatures, forming azo-dyes which contain the ψ-aziminobenzene group. The reduction proceeds further on warming, the nitrogen ring being broken and *o*-diamines being produced. C. H. D.

Distribution of Nitrogen in the Proteid Molecule. Theodor Gümbel (*Beitr. chem. Physiol. Path.*, 1904, 5, 297—312. Compare Hausmann, Abstr., 1899, i, 653; 1900, i, 317; Kutscher, 1901, i, 107; Osborne and Harris, 1903, i, 585).—Osborne and Harris's conclusion that Hausmann's method is convenient and yields approximate results is supported by a number of experimental results. For the estimation of amide-nitrogen, distillation under reduced pressure at 40° is recommended (Schwarzchild, *Beitr. chem. Physiol. Path.*, 1903, 4, 155). The solubility of arginine phosphotungstate is less in the presence of an excess of phosphotungstic acid, and even when a solution (1 in 700) of 0·1 gram of arginine is precipitated and washed, the maximum loss is only some 10 per cent. Lysine behaves similarly to arginine, but histidine is appreciably soluble in a large excess of phosphotungstic acid. The precipitated phosphotungstates are at first flocculent and afterwards crystalline, and in the latter condition appear to be less soluble than in the former. The errors introduced by the precipitation of the phosphotungstates of monamino-acids and of melanine with the diaminophosphotungstates are small.

The distribution of nitrogen in serum albumin (15·93 per cent. of nitrogen) is amide, 1·01; melanine, 0·16; diamino, 5·30; monoamino, 9·61. The values for edestin agree with those of Hausmann and of Osborne and Harris. For keratin, amide, 1·17; melanine, 0·42; diamino, 2·95; monoamino, 11·81. For cartilage, amide, 1·35; melanine, 0·36; diamino, 1·35; monoamino, 7·95. For potassium chondrotinsulphate, amide, 35·27; melanine, 9·54; diamino, 32·78; and monoamino, 21·57 per cent. J. J. S.

Decomposition Products of Proteids containing Sulphur. Kalle & Co. (D.R.-P. 146947).—When proteid solutions or suspensions are heated with alkali sulphides, only traces of ammonia are pro-

duced, and compounds containing a larger quantity of sulphur than the original proteids are obtained. The product generally contains two compounds, one of which is precipitated from a solution of the sodium salt by acids, whilst the other is not. The alkali sulphide is best removed by dialysis. The product from egg albumin contains 15—15·5 per cent. of nitrogen and 2—2·5 per cent. of sulphur, that from casein contains 3—5·5 per cent. of sulphur. These compounds have the property of precipitating the heavy metals in a colloidal form from solutions of their salts. C. H. D.

Action of Sulphur on Proteids. ARTHUR HEFFTER and MAX HAUSMANN (*Beitr. chem. Physiol. Path.*, 1904, 5, 213—233. Compare Rösing, Abstr., 1892, 741).—The action of clear white of egg on sulphur has been studied. In many cases, 2 per cent. of sodium fluoride was added; this did not destroy the reducing action, and preserved the albumin. Other preservatives, such as toluene and chloroform, do not affect the evolution of hydrogen sulphide, nor does hydrocyanic acid. The temperature has but little influence, the addition of acid until the reaction with Congo-red is given tends to lessen the evolution of hydrogen sulphide, but the activity may be again restored by the addition of alkali. Saturation with sodium, potassium, or ammonium chloride, ammonium nitrate, or magnesium sulphate does not completely inhibit the evolution of hydrogen sulphide, whereas precipitation by saturation with ammonium sulphate or phosphate does. The evolution of gas is facilitated by the addition of a small amount ($\frac{1}{5}$ vol.) of alcohol, as this assists the solution of the sulphur, but is completely stopped by a large excess (2 vols.) of alcohol. The precipitate obtained by the addition of a large volume of alcohol reduces sulphur on the addition of water, whereas the clear filtrate from the precipitated albumin does not. Similarly, albumin precipitated by other reagents (acetic acid, phenol, or potassium ferrocyanide) has not lost its power of reducing sulphur. A few reagents, such as ferric chloride and copper sulphate, can completely destroy the property. Hydrolysis with pepsin hydrochloric acid has a similar effect.

The constituent of white of egg, which has the property of reducing sulphur, appears to be crystallised ovalbumin. White of egg also reduces arsenates to arsenites, nitrates to nitrites, iodates to iodides.

Selenium, phosphorus, sulphites and acid sulphites, methylene-blue, and indigotinsulphonic acid are not reduced; thiosulphates liberate hydrogen sulphide.

Cow's milk, as a rule, reduces sulphur to hydrogen sulphide; the reaction in many cases only begins after one or two days, and may be prevented by the addition of antiseptics. The evolution of sulphide in this case is attributed to the agency of micro-organisms.

Blood also reduces sulphur, and the active substance appears to be a compound soluble in water which is contained in the blood corpuscles.

Rösing's results with various organs (brain, liver, pancreas, &c.) are confirmed. The evolution of gas with calf's liver does not vary appreciably during the first 4—6 hours. When kept for 7 days, the

amount of hydrogen sulphide is found to be much smaller. Boiling decreases the amount of sulphide evolved.

The globulins of white of egg and of blood serum, fibrin, serum albumin, the proteids of milk, and other secretions have no reducing action on sulphur.

The hydrogen sulphide obtained by boiling proteids with sulphur and water may have an entirely different origin, since sulphur and boiling water and proteids and boiling water evolve hydrogen sulphide.

The oxidation is regarded not as a fermentation process nor as analogous to autoxidation, but as a mere removal of hydrogen atoms from the molecule of the substance oxidised. This view is confirmed by the fact that numerous carbon compounds, namely, benzyl mercaptan, thiophenol, thioglycollic acid, and sodium thioglycollate are readily oxidised by sulphur, evolving hydrogen sulphide. J. J. S.

Animal Glutins. III. Reactions with Salt Solutions. Wl S. Sadikoff (*Zeit. physiol. Chem.*, 1904, 41, 15—19. Compare this vol., i, 125, 126; Pauli, Abstr., 1900, i, 265; 1902, ii, 388).—The solubilities of commercially pure gelatin, sinew trypsinglutin A, nasal glutein, tracheal glutein, and aural glutein in the following solutions have been investigated: potassium chloride, nitrite, and cyanide, sodium chloride, potassium bromide, iodide, thiocyanate, nitrate, and chlorate, ammonium nitrate and chloride, magnesium chloride, zinc chloride. The solutions employed were 50 per cent. solutions or cold saturated solutions. The different glutins are soluble in all the solvents with the exception of the four first named. Of these four, only sodium chloride dissolves commercial gelatin, none dissolve sinew trypsinglutin A. The three gluteins are soluble in all the reagents.

Potassium nitrite and chloride solutions dissolve part of commercial gelatins, but the remainder is insoluble.

Heating the dry glutins decreases their solubility in salt solutions. J. J. S.

Oxidation of Gelatin by Permanganate. Goswin Zickgraf (*Zeit. physiol. Chem.*, 1904, 41, 259—272. Compare Abstr., 1903, i, 666; Lossen, *Annalen*, 201, 369; Pommerrenig, Abstr., 1902, ii, 274).—It has been found that in the partial oxidation of gelatin by calcium permanganate the amount of guanidine increases as the biuret reaction diminishes. The conclusion is drawn that the biuret reaction of gelatin is due to the presence of an arginine residue in the molecule. J. J. S.

Protagon, Choline, and Neurine. Wilhelm Cramer (*J. Physiol.*, 1904, 31, 30—37).—The objections urged by Wörner and Thierfelder and by Lesem and Gies against the chemical individuality of protagon are not conclusive. Analyses give constant results when the material is prepared in various ways; a new method of preparation is given in the present paper. Protagon is not decomposed by warm ether or boiling alcohol. By decomposition with baryta water, choline is the only base formed. Choline can be readily

distinguished from neurine by their chromates, choline chromate being easily soluble, and neurine chromate almost insoluble in cold water.

W. D. H.

Pepsin-glutinopeptone. W. SCHEERMESSER (*Zeit. physiol. Chem.*, 1904, **41**, 68—98. Compare Siegfried, Abstr., 1903, i, 782).—Peptones are not immediately produced during the peptic digestion of gelatin; they appear to be formed indirectly from albumoses and make their appearance during the third day. A new peptone, *pepsin-glutinopeptone*, has been isolated by the iron alum method from the products of digestion of gelatin. Its molecular formula is $C_{23}H_{39}O_{10}N_7$, and it has $[\alpha]_D - 77—78°$ approximately. It gives the biuret reaction readily, but not Molisch's reaction, and yields no precipitate with mercuric chloride, lead acetate, silver nitrate, potassium ferrocyanide, acetic acid, or metaphosphoric acid. Precipitates are obtained with tannic acid and in concentrated solutions with phosphotungstic acid. *Barium* and *zinc* salts have been prepared. On hydrolysis with 33·3 per cent. sulphuric acid, the peptone yields arginine, lysine, glutamic acid, and glycine.

The distribution of the nitrogen is as follows: amido-nitrogen, 0. Basic nitrogen, 25; of this 15·6 is due to arginine and 9·4 to lysine. Monoamino-nitrogen, 70 per cent., of which 10—11 is due to glutamic acid.

J. J. S.

Monoamino-acids from Salmin. EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1904, **41**, 55—58. Compare Kossel, this vol., i, 211).—The following monoamino-acids have been isolated from the hydrolytic products from salmin by Fischer's esterification method: alanine, leucine, pyrrolidine-2-carboxylic acid, and probably phenylalanine and aspartic acid.

J. J. S.

Colouring Matter of Blood. I. J. HETPER and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1904, **41**, 38—41).—Mörner's β-hæmin is not a pure compound, its composition varies considerably with the physical conditions under which it is prepared, and it appears to be a mixture of acethæmin with several of its ether derivatives.

J. J. S.

Relationship of Chlorophyll and Hæmoglobin. LEON MARCHLEWSKI (*Pflüger's Archiv*, 1904, **102**, 111—115. Compare Abstr., 1902, i, 387; 1903, ii, 677).—Largely polemical. A discussion of the results previously obtained by the author and others. The close relationship of the two pigments is regarded as certain, and the author maintains his priority in proving it.

W. D. H.

Lability and Activity of Enzymes. OSCAR LOEW (*Pflüger's Archiv*, 1904, **102**, 95—110).—A theoretical discussion of the meaning of the term lability, and the mode of action of enzymes. Lability is increased by the amino-groups present.

W. D. H.

The Enzyme Melibiase, and Comparative Studies of Maltase, Invertase, and Zymase. Arminius Bau (*Chem. Centr.*, 1904, i, 734; from *Zeit. Spiritusindustrie*, 27, 2—3, 9—10, 19—21, 29—31).—The effect of chemical reagents on melibiase and other yeast enzymes has been determined. Melibiase is contained in bottom fermenting yeast, and by its action melibiose is converted into dextrose and *d*-galactose. Contrary to Lindner's conjecture (*Woch. Brau.*, 17, 747) melibiase was found to resist the action of chemicals better than maltase, whilst invertase was the least affected and zymase the most. The activity of melibiase is not destroyed by drying, and, in one case, had not disappeared after remaining more than $5\frac{3}{4}$ years in the dry state; in this condition it may also be heated for a long time at 110°. Maltase prepared from either bottom or top fermenting yeast may also be dried (Bokorny, Abstr., 1901, i, 437); the activity of invertase is still less impaired by drying, whilst zymase is considerably more affected. The temperatures above which the zymases cease to be active were determined by experiments on yeast; for maltase, melibiase, and invertase these temperatures were found to be 55°, 70°, and 75° respectively. At 50°, the action of melibiase is at a maximum. Of the oxydases, lipases, and proteolytic enzymes also contained in the yeast cell, only the last have any action on the enzymes mentioned above. Invertase offers the greatest resistance to the action of proteolytic enzymes, maltase less than melibiase, and zymase the least of all. Melibiase occurs also in all the bottom fermenting yeasts of the Frohberg and Saaz type, but is not present in top fermenting, wine, and wild yeasts. Other sources of melibiase are also mentioned in the original paper. E. W. W.

Preparation of Phenylsilicon Compounds. Walther Dilthey and F. Eduardoff (*Ber.*, 1904, 37, 1139—1142. Compare Kipping, Proc., 1904, 19, 15).—When an ethereal solution of silicon tetrachloride (1 mol.) and magnesium phenyl bromide (8 mols.) is heated for three days on the water-bath, the principal product is triphenylsilicol, $SiPh_3{\cdot}OH$, which crystallises in fern-like groups of prisms and melts at 155° (compare Polis, Abstr., 1886, 618, and Kipping and Lloyd, Trans., 1901, 79, 449). When the compounds are only allowed to react at the ordinary temperature for a few hours, the principal product is *diphenylsilicol*, $SiPh_2(OH)_2$, which crystallises from benzene in silky needles, melts at 138—139°, and dissolves readily in ether or chloroform, sparingly in light petroleum, and is insoluble in water. It loses 1 mol. of water on fusion and yields a gelatinous mass, which appears to be Kipping and Lloyd's diphenylsilicoketone, CPh_2O. C. H. D.

Organic Chemistry.

Action of Water on Trimethylene Dibromide and of Sulphuric Acid on Trimethylene Glycol. MARCELLUS RIX (*Monatsh.*, 1904, 25, 267—276. Compare Lieben, Abstr., 1902, i, 336).—When heated in a sealed tube at 170° with 12 volumes of water, trimethylene dibromide yields propaldehyde, acetone, and trimethylene glycol. If less water is used, part of the propaldehyde condenses to methylethylacraldehyde. With 6 volumes of water at 150° for 30 hours, trimethylene dibromide yields phorone and mesitylic oxide, in addition to the above products.

Acetone, propaldehyde, and methylethylacraldehyde are obtained when trimethylene glycol is heated with dilute sulphuric acid at 170°. The glycol remains unchanged when heated with water at 215—220° for 2 days. G. Y.

Purifying and Characterising Alcohols. LOUIS BOUVEAULT (*Compt. rend.*, 1904, 138, 984—985).—The methods hitherto employed for purifying and characterising alcohols are unsatisfactory, owing to the fact that the alcohols are generally liquids, and yield liquid (esters) or readily soluble solid derivatives (phenylurethanes). The method described in this paper is free from these disadvantages, but is limited in application to those alcohols which form esters with pyruvic acid, and consists in converting the pyruvates into the semicarbazones, $NH_2\cdot CO\cdot NH\cdot N:CMe\cdot CO_2R$, which are insoluble in water, slightly so in light petroleum, and fairly soluble in the other organic solvents, from which they crystallise easily; on treatment with alcoholic potassium hydroxide, the corresponding alcohol is regenerated. The following derivatives of primary or secondary alcohols were prepared: *ββ-dimethylpropyl pyruvate semicarbazone*, melting at 168°; *octyl pyruvate semicarbazone*, melting at 118—119°; *benzyl pyruvate semicarbazone*, melting at 176°; *phenylpropyl pyruvate semicarbazone*, melting at 143°; *hexahydrobenzyl pyruvate semicarbazone*, melting at 182°; and *βζ-dimethyloctyl pyruvate semicarbazone*, melting at 124°. The tertiary alcohols are decomposed on boiling with pyruvic acid, forming water and an ethylene hydrocarbon, the reaction affording a convenient method of preparing the latter. M. A. W.

Transformation of Amides into the Corresponding Primary Alcohols. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1904, 39, 418—420).—A claim for priority (compare Bouveault and Blanc, this vol., i, 213). W. A. D.

Hydrates of Methyl Alcohol and of Acetone. EUGÈNE VARENNE and L. GODEFROY (*Compt. rend.*, 1904, 138, 990—992).—The authors have measured the viscosity of aqueous solutions of methyl alcohol and of acetone by means of their constant pressure capillary viscosimeter [chronostiliscope] (compare this vol., i, 2;

ii, 160); the curves obtained by plotting these values as ordinates against the percentage composition of the mixture as abscissæ, indicate the existence of hydrates at singular points. Methyl alcohol forms six hydrates, the two most important being $CH_4O,3H_2O$ and CH_4O,H_2O; the others are $CH_4O,2H_2O$; $CH_4O,5H_2O$; $CH_4O,8H_2O$, and $CH_4O,20H_2O$. Acetone forms three distinct hydrates with $3H_2O$, $4H_2O$, and $8H_2O$ respectively, and probably one having $34H_2O$.

M. A. W.

Composition of the Fusel Oil obtained in the Distillation of Acorns. TH. RUDAKOFF and A. ALEXANDROFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 207—219).—The fusel oil obtained in distilling acorns is qualitatively similar to that yielded by potato spirit, from which, however, it differs in quantitative composition. It contains about 2·7 per cent. of normal propyl alcohol, 9·8 of *iso*butyl alcohol, 87·4 of amyl alcohol containing about one-fourth of its weight of the active modification, together with very little normal hexyl alcohol, acetaldehyde, compound esters, and furfuraldehyde.

T. H. P.

Formation of Alcohols by Reduction of Acid Amides. RUDOLF SCHEUBLE and EMMO LOEBL (*Monatsh.*, 1904, **25**, 341—353. Compare this vol., i, 3).—Reduction with sodium and amyl alcohol of palmitamide and stearamide leads to the formation of hexadecyl alcohol and octodecyl alcohol respectively. Suberamide is reduced by sodium and amyl alcohol to octomethylene glycol and octomethylenediamine. Lauramide is reduced in the same manner to dodecyl alcohol and dodecylamine, and a *substance* which melts at 195°. Lauramide is also reduced, but not so completely, by sodium and ethyl alcohol.

G. Y.

Action of Sulphuric Acid on Butan-αγ-diol. VIKTOR KADIERA (*Monatsh.*, 1904, **25**, 332—340. Compare Lieben, Abstr., 1902, i, 336).—αγ-Dihydroxybutane (butan-αγ-diol) is not changed when heated with water at 200° for 8 hours. When heated with twice its volume of 10 per cent. sulphuric acid at 190° for 8 hours, αγ-dihydroxybutane yields ethylene, *n*-butaldehyde, methyl ethyl ketone, and α-ethyl-β-propylacraldehyde (Raupenstrauch, Abstr., 1887, 794).

When αγ-dihydroxybutane is allowed to remain in contact with 50 per cent. sulphuric acid, cooled by ice, butaldehyde and methyl ethyl ketone, but no ethylpropylacraldehyde, are formed.

G. Y.

Volatility of Carbon Compounds. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1904, 42—63. Compare Abstr., 1903, ii, 8).—*Methyl* iso*propyl ether*, prepared by the interaction of methyl iodide with sodium *iso*propoxide, boils at 32·5° under 777 mm. pressure, has a sp. gr. 0·7347 at 20° and n_D 1·35756 at 20°. *Methyl* tert.-*butyl ether*, prepared similarly or by Reboul's method (Abstr., 1881, 1025), when methyl ψ-butyl ether and *iso*butylene are also formed, boils at 54—55°, has a sp. gr. 0·7578 and n_D 1·37566 at 20°. iso*Propyl* tert.-*butyl ether*, obtained by the action of *tert.*-butyl chloride on *iso*propyl alcohol or by heating a mixture of the two corresponding

alcohols with sulphuric acid, is a very mobile liquid, boils at 75—76° under 768 mm. pressure, has a sp. gr. 0·7734 at 20°, and n_D 1·3858. Ethyl *tert.*-butyl ether boils at 70° under 758 mm. pressure, has sp. gr. 0·7519 at 20° and n_D 1·3794 at 20° (compare Reboul, *loc. cit.*, and Mamontoff, *J. Russ. Phys. Chem. Soc.*, 1897, 29, 230).

The boiling point in this series of ethers is dependent principally on the molecular weight; starting with methyl ether, the substitution of one hydrogen atom in one of the methyl groups by methyl leads to a rise in boiling point, but further similar substitutions produce, as the series is ascended, progressively smaller effects; the influence of the substituent group in elevating the boiling point decreases with the extent of alkylation, which has already been effected in the same group; thus, whereas the difference between the boiling points of ethyl and of propyl ethers is 33—34°, that between the boiling points of the respective isomerides methyl, propyl, and ethyl *tert.*-butyl ethers is 38°. The position in which substitution occurs appears to have but little effect on the boiling point. The boiling points of mixed ethers are not equivalent to the means of those of the two corresponding simple ethers, but are usually higher, and the difference is the more marked as the masses of the two alkyl radicles of the mixed ether are dissimilar. T. A. H.

Halogen Ether Oxides, $RO(CH_2)_nX$; their Magnesium Compounds, $RO·[CH_2]_n·MgX$; New Syntheses in the Tetramethylene Series. JULES HAMONET (*Compt. rend.*, 1904, 138, 975—977).—*δ-Bromo-α-amyloxybutane*, $C_5H_{11}·O·[CH_2]_3·CH_2Br$, obtained by the action of two mols. of hydrogen bromide on 1 mol. of αδ-diamyloxybutane (compare Abstr., 1901, i, 187) in the cold, is a colourless liquid with an agreeable fruity odour, boils at 114—115° under 16 mm. pressure, does not crystallise when cooled in a mixture of solid carbon dioxide and ether, and has a sp. gr. 1·14 at 18°. *δ-Iodo-α-amyloxybutane*, $C_5H_{11}·O·[CH_2]_3·CH_2I$, prepared by the action of sodium iodide on the preceding compound in alcoholic solution, is a slightly coloured liquid boiling at 128—129° under 16 mm. pressure and having a sp. gr. 1·523 at 18°. This method of preparing halogen alkyloxy-compounds of the type $RO(CH_2)_nX$ appears to be a general one, *αε-diamyloxypentane*, $(CH_2)_5(OC_5H_{11})_2$, yielding ε-bromo-α-amyloxypentane, $(C_5H_{11}O)(CH_2)_5Br$, and βε-diamyloxyhexane giving a corresponding derivative.

These halogen alkyloxy-compounds react with magnesium to form compounds of the type $RO·[CH_2]_n·MgX$, of which the following were prepared: $OMe·[CH_2]_3·MgI$ from γ-iodo-α-methoxypropane,

$$C_5H_{11}·O·[CH_2]_3·MgI$$

from γ-iodo-α-amyloxypropane, $C_5H_{11}·O·[CH_2]_4·MgBr$ from δ-bromo-α-amyloxybutane, and $C_5H_{11}·O·[CH_2]_5·MgBr$ from ε-bromo-α-amyloxypentane.

αδ-Diamyloxybutane (compare Abstr., 1901, i, 187) is obtained by the action of amyloxybromomethane on the magnesium derivative of γ-iodo-α-amyloxypropane according to the equation:

$$C_5H_{11}O·[CH_2]_3·MgI + Br·CH_2·OC_5H_{11} = MgBrI + (CH_2)_4(OC_5H_{11})_2;$$

αδ-dimethoxybutane, $(CH_2)_4(OMe)_2$, prepared by a similar method, is a

very mobile liquid boiling at 132—133° under 760 mm. pressure, and has a sp. gr. 0·859 at 18°. M. A. W.

Theory of Saponification. FRANZ GOLDSCHMIDT (*Zeit. Elektrochem.*, 1904, 10, 221—222).—Euler (Abstr., 1901, ii, 307) concluded that the hydrolysis of esters points to their dissociation into negative alkoxyl ions and positive ions of the formula R·CO. The author has independently reached the same conclusion by considering the saponification of fats. Sodium ethoxide reacts with a fat instantaneously, giving the ethyl ester of the fatty acid and the sodium salt of glycerol. Alcoholic potash gives the same result, the ethyl ester of the fatty acid subsequently undergoing saponification slowly. These changes are best explained by assuming that the fatty acid radicle behaves as a positive ion. These positive ions would be derived from a hypothetical base containing quadrivalent oxygen, the electrolytic dissociation of which is represented thus:

$$R\cdot C{:}O\cdot OH \longrightarrow R\cdot C{:}O^{\bullet} + OH',$$

whereas the dissociation of the ordinary acid form is represented by the equation $R\cdot C{<}^{O}_{OH} \longrightarrow \left(R\cdot C{<}^{O}_{O}\right)' + H^{\bullet}$. From this point of view, acetyl chloride is regarded as the chloride of the basic ion $CH_3\cdot CO^{\bullet}$, acetic anhydride as a compound of the ions $CH_3\cdot CO^{\bullet}$ and $CH_3\cdot CO\cdot O'$, or as acetyl acetate. T. E.

Salts of Antimony with Organic Acids. III. EDUARD JORDIS (*Zeit. angew. Chem.*, 1904, 17, 330—334. Compare Abstr., this vol., i, 216, 282).—Again a theoretical paper, a reply to Moritz and Schneider (Abstr., 1902, i, 703). A. McK.

Solubility of Some Salts of the Lower Fatty Acids. H. STANLEY (*Chem. News*, 1904, 89, 193).—The author has determined the solubility of barium and strontium formates and gives the results both in tabular form and in curves. Whilst the curve for calcium formate is practically a straight line (Trans., 1902, 81, 355), those for these two salts are more pronounced. That for strontium formate, which crystallises with $2H_2O$, shows a break at a temperature of 83°, the solubility then decreasing as the temperature rises. W. P. S.

Ferric Aceto-compounds. ARTHUR ROSENHEIM and PAUL MÜLLER (*Zeit. anorg. Chem.*, 1904, 39, 175—186).—Whilst normal ferric acetate, which is acted on by water to form the salt, $Fe(OH)_2\cdot C_2H_3O_2$, is prepared by dissolving ferric hydroxide in aqueous acetic acid, the action is different when glacial acetic acid is used. When ferric hydroxide is boiled with glacial acetic acid for several hours, the undissolved product is *diferric penta-acetohydroxide*, $Fe_2(C_2H_3O_2)_5\cdot OH$, which crystallises in dark red, microscopic plates. Its aqueous solution, which is bluish-red and odourless, is hydrolysed at the ordinary temperature, or more readily on warming, with formation of colloidal ferric hydroxide and acetic acid. The solution remains clear on being boiled, but the addition of an electrolyte, such as sodium chloride or sodium sulphate, causes the quantitative precipitation of

ferric hydroxide. The course of the hydrolysis in the cold was followed by determining the lowerings of the freezing point and the molecular conductivities of the solutions after definite periods. That a complex cathion exists in solutions of diferric penta-acetohydroxide was indicated by the absence of a colour change in presence of potassium thiocyanate.

Ferric diacetochloride, $Fe(C_2H_3O_2)_2Cl$, prepared from ferric chloride and glacial acetic acid, crystallises in reddish-brown needles. Concentrated aqueous solutions are dark red in colour and become yellow on dilution. Solutions which, to begin with, contain the complex cathion, $Fe(C_2H_3O_2)_2$ and the anion Cl, suffer hydrolytic dissociation with formation of ferric hydroxide and acetic acid when the solution is boiled; on cooling, the solution again contains the complex cathion along with colloidal ferric hydroxide. This view was borne out by qualitative observations and by measurements of the lowering of the freezing point on the one hand, and by conductivity determinations on the other.

Ferric diacetobromide, $Fe(C_2H_3O_2)_3Br$, prepared from ferric bromide and glacial acetic acid, forms dark brown needles and is more soluble in water than the chloride. In its solutions, the complex cathion, $Fe(C_2H_3O_2)_2$, is again present.

Tetraferric ennea-acetonitrate, $Fe_4(C_2H_3O_2)_9(NO_3)_3$, prepared by allowing a solution of ferric nitrate in boiling glacial acetic acid to crystallise, separates in ruby-red prisms. When more ferric nitrate is used, brown needles of *diferric penta-acetonitrate*, $Fe_2(C_2H_3O_2)_5NO_3,H_2O$, separate. It is probable that when those nitrates are dissolved in water, the ion is present in the complex cathion.

Ferric diformyl chloride, $Fe(HCO_2)_2Cl,1\frac{1}{2}H_2O$, prepared from ferric chloride and anhydrous formic acid, forms a bright yellow, crystalline powder. A. McK.

Action of Chlorine on Anhydrous Acetates. ALBERT COLSON (*Bull. Soc. chim.*, 1904, **31**, 422—430).—A *résumé* of work already published (Abstr., 1903, i, 396, 456, 601; and this vol., i, 3 and 134). T. A. H.

Decomposition of Some Trichloro- and Tribromo-acetates in Acetone. L. D. KOBOZEFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 247—255).—The author's investigations on the products obtained by the decomposition of potassium hydrogen trichloro- and tribromo-acetates in acetone solutions show that the first change taking place is according to the equation: $CX_3\cdot CO_2H,CX_3\cdot CO_2K = CX_3H + CO_2 + CX_3\cdot CO_2K$, where X represents chlorine or bromine. When all the free acid of the acid salt has been decomposed in this way, the water present in the acetone acts on the normal salt remaining, according to one of the following equations: (1) When the water is in excess, $CX_3\cdot CO_2K + H_2O = CX_3H + KHCO_3$; (2) when insufficient water is present, $2CX_3\cdot CO_2K + H_2O = 2CX_3H + K_2CO_3$. Finally, the chloroform or bromoform, under the influence of potassium carbonate, reacts with the acetone yielding trichloro- or tribromo-trimethylcarbinol. T. H. P.

Decomposition of Trichloroacetic Acid and Some of its Salts in Aqueous Solution. WLADIMIR F. TIMOFÉEFF and L. D. KOBOZEFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 255—275).—In the decomposition of trichloroacetic acid in aqueous solution into chloroform and carbon dioxide, the constant of the velocity of the reaction, which is of the first order, diminishes very considerably with increase of concentration of the acid and becomes almost zero for very concentrated solutions. From this it is seen that the reaction proceeds at the expense of the active molecules of acid. The addition to the solution of trichloroacetic acid of an equivalent quantity of hydrochloric acid causes a large decrease in the constant; thus, at 87°, K falls from 0·0054 to 0·0036 (with hydrochloric acid). In the case of salts of trichloroacetic acid, which undergo a similar decomposition in aqueous solution, the water present must take part in the reaction in order to supply the hydrogen required for the formation of chloroform, and it is hence probable that water acts also in the decomposition of the acid. With potassium and sodium trichloroacetates, the velocity constant of decomposition falls rapidly as the reaction proceeds; that this is due to the accumulation of a salt of carbonic acid was shown by carrying out an experiment in presence of potassium carbonate, in which case K was found to be considerably less than before, but much more constant. To eliminate the influence of dissolved products of the reaction, the decomposition of barium trichloroacetate was studied, K in this case being found to be quite constant.

The decomposition of tribromoacetic acid in aqueous solution is also a reaction of the first order, and the constant is here much greater than with the chloro-acid at the same temperature.

According to the electrolytic dissociation theory, these decompositions would be expressed by the scheme: $CCl_3\cdot\overset{-}{COO} + \overset{+}{H}(K,Na,ba) + H_2O = CHCl_3 + - - -$, which would be an equation of the second (and, for the barium salt, perhaps the third) order; so that, like certain others, this reaction is not explained by the above theory.

It is, however, possible that the reaction may take place in the three phases: (1) preliminary hydration of the $CCl_3\cdot COO$ ions to $CCl_3\cdot CO(OH)_2\cdot$, (2) decomposition of the latter at high temperatures into $CHCl_3 + CO_2 + \overset{-}{OH}$, and (3) combination of the $\overset{-}{OH}$ and $\overset{+}{H}$ ions, and that only the second of these determines the velocity.

T. H. P.

Asymmetric Synthesis. WILLY MARCKWALD (*Ber.*, 1904, 37, 1368—1370).—A reply to Cohen and Patterson (this vol., i, 366). A synthesis is "asymmetric" when, starting from a symmetrical compound, an asymmetrical product is obtained without the aid of any process of separation of isomerides. In the synthesis of active *l*-valeric acid from symmetrical methylethylmalonic acid (this vol., i, 221), the latter is converted quantitatively into the brucine salt, from which the active acid is obtained quantitatively. The presence of asymmetric ions is not essential, since the formation of the brucine salt takes place equally well in non-dissociating solvents. C. H. D.

Combinations of Titanic Acid with Lactic Acid. Carl Dreher (D.R.-P. 149577).—Titanic acid dissolves only sparingly in lactic acid, but more readily in the presence of lactates of the alkalis or of the alkaline earths. A larger proportion of lactic acid and lactates is required to obtain a clear solution of titanic acid than in the corresponding case of the oxalates. The acid products obtained by evaporating the solutions are highly hygroscopic; alkalis convert them into neutral solutions or salts having a constitution approximating to the formula $TiO_2,C_3H_6O_3,3MC_3H_5O_3$ or $TiO_2,4MC_3H_5O_3$, according to the proportion of alkali employed. C. H. D.

Active Lactic and Malic Esters. Eugène Wassmer and Philippe A. Guye (*J. Chim. Phys.*, 1903, i, 257—288).—The density, refraction, and dispersion, and the specific and molecular rotation and rotatory dispersion were determined for a number of esters. The first series consisted of the following derivatives of ethyl malate: ethyl propionyl-, butyryl-, hexoyl-, heptoyl-, octoyl-, pelargonyl-, and decoyl-malates. In this series, the specific rotation diminishes throughout from the propionyl- to the decoyl-compound, but the molecular rotation passes a maximum at the butyryl compound, after which it tends to a final limiting value. This was the case for all temperatures, and for light of various wave-lengths. The specific rotatory dispersion decreases as the series is ascended, but the molecular dispersion, whilst varying but slightly, passes through a maximum. The method of preparation of the active lactates is described. The second series of compounds consisted of the *l*- and *d*-propyl lactates, *d*-butyl lactate, *l*-*iso*butyl lactate, *l*-heptyl lactate, and *l*-octyl lactate. Owing to slight impurity in the ammonium zinc lactate from which the esters were obtained, the values for the rotation were multiplied by a correction factor. The specific rotation has a maximum for the octyl ester, the molecular rotation has no maximum and tends to a limiting value. The rotatory dispersion is almost equal for all the compounds, and is almost independent of temperature. The third series consisted of the acetyl, propionyl, butyryl, and benzoyl derivatives of *l*-*iso*butyl lactate. In these, the specific rotation steadily decreases, the molecular rotation passes a maximum for the propionyl compound, whilst as in other series the dispersion is almost the same for the three allied compounds.

L. M. J.

Lactone of Hydroxycrotonic Acid and the γ-Substituted Crotonic Acids. Robert Lespieau (*Compt. rend.*, 1904, 138, 1050—1051).—*βγ-Dibromobutyramide*, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, prepared by dissolving the corresponding nitrile in fuming hydrobromic acid, melts at 86°, and when treated with dilute aqueous potassium hydroxide loses the elements of hydrogen bromide to form *γ-bromocrotonamide*, $CH_2Br{\cdot}CH{:}CH{\cdot}CO{\cdot}NH_2$, which melts at 110°. *γ-Bromocrotononitrile*, $CH_2Br{\cdot}CH{:}CH{\cdot}CN$, prepared by heating βγ-dibromobutyronitrile (compare Abstr., 1903, i, 547), is a viscid liquid boiling at 84° under 12 mm. pressure and melting at −14°; when hydrolysed by hydrobromic acid, it yields βγ-dibromobutyric acid, whilst with hydrochloric acid, it yields βγ-dichlorobutyric acid, the

acid playing the triple *rôle* of saturating the ethylenic linking, hydrolysing the nitrile, and substituting chlorine for the bromine in the γ position. It is probable that in these reactions a lactone is first formed, which reacts with the halogen acid to give the substituted butyric acid, for if $\beta\gamma$-dichlorobutyric acid is heated for 30 minutes at 200—215° in a slow current of air, the *lactone* of *hydroxycrotonic acid*, $\begin{matrix}CH\cdot CH_2\\ \| \\ CH—CO\end{matrix}\!\!>\!O$, is produced; it is a viscid liquid boiling at 95—96° under 13 mm. pressure and melting at +4°, is soluble in water and precipitated by potassium carbonate, reduces ammoniacal silver nitrate with the formation of a mirror, slowly decolorises bromine, and gives with concentrated hydrobromic acid $\beta\gamma$-dibromobutyric acid (compare Hill and Cornelison, Abstr., 1894, i, 319). M. A. W.

Ethyl Bromonitromalonate. RICHARD WILLSTÄTTER and VALENTIN HOTTENROTH (*Ber.*, 1904, **37**, 1775—1787).—*Methyl bromonitromalonate*, $NO_2\cdot CBr(CO_2Me)_2$, is a colourless neutral oil boiling at 133° under 16 mm. pressure; the *ethyl* ester boils at 136—137° under 11 mm. pressure. *Methyl dihydroxymalonate* is deposited from benzene in colourless, columnar crystals, and from light petroleum in colourless needles melting at 77·5°; the *ethyl* ester crystallises in large, transparent plates melting at 57°; both compounds are obtained on heating the corresponding alkyl bromonitromalonates. The *dimethylamine* salt of methyl bromonitromalonate crystallises in faint yellow prisms melting at 150°, and is prepared by the action of dimethylamine in cold ethereal solution. *Bromodimethylamine*, NMe_2Br, is formed at the same time, but is better prepared (Berg's method for chlorodimethylamine, Abstr., 1895, ii, 297) by the interaction of sodium hypobromite and dimethylamine hydrobromide in cold aqueous solution. It is a yellow oil boiling at 64—66°.

Ethyl bromonitromalonate and ammonia interact in ethereal solution forming the ammonium salt of ethyl nitromalonate described by Franchimont and Klobbie (Abstr., 1889, 1143). By the interaction of methyl bromonitroacetate and concentrated aqueous ammonia, the *ammonium* salt of *bromonitroacetamide* is formed, the free amide crystallises from benzene or light petroleum in colourless needles or thin prisms melting at 80—81°. *Chloroiodoacetamide* was prepared by the action of ammonia on methyl chloroiodoacetate and subsequent fractional crystallisation; it forms colourless, glistening needles melting at 140—141°. E. F. A.

α-Methylparaconic Acid. FRITZ FICHTER and ERNST RUDIN (*Ber.*, 1904, **37**, 1610—1614).—Ethyl pyrotartrate and ethyl formate condense in presence of sodium ethoxide, forming *ethyl β-hydroxymethylenepyrotartrate*, $OH\cdot CH{:}C(CO_2Et)\cdot CHMe\cdot CO_2Et$, together with an isomeride, which may be *ethyl β-formylpyrotartrate*,

$$CHO\cdot CH(CO_2Et)\cdot CHMe\cdot CO_2Et;$$

they could not be completely separated.

Sodium amalgam reduces the hydroxymethylene compound only, forming *ethyl α-methylparaconate*, $CO\!<\!\begin{matrix}O\cdot CH_2\\ CHMe\end{matrix}\!>\!CH\cdot CO_2Et$, which boils

at 145—150° under 14 mm. pressure. *a-Methylparaconic acid*, $C_6H_8O_4$, crystallises from absolute ether in large, transparent prisms, melts at 104°, and dissolves readily in water, alcohol, or chloroform, sparingly in ether or benzene. The *zinc* salt forms transparent, glistening prisms. On neutralising a hot solution of the acid with lime, hard crusts of *calcium a-methylitamalate*, $C_6H_8O_5Ca$, separate. a-Methylparaconic acid decomposes partially on distillation, forming pyrocinchonic anhydride, but not vinylpropionic acid.

In the hydrolysis of ethyl a-methylparaconate with baryta, the barium salt of an acid, $C_8H_{12}O_5$, is obtained. The acid crystallises in short prisms, melts at 151°, and is probably *β-ethoxymethylenepyrotartaric acid*, $OEt\cdot CH{:}C(CO_2H)\cdot CHMe\cdot CO_2H$. C. H. D.

a-Methyl-Δ^{β}-pentenoic Acid. Fritz Fichter and Ernst Rudin (*Ber.*, 1904, **37**, 1615—1619).—Sodium amalgam reduces ethyl acetopyrotartrate, $CH_3\cdot CO\cdot CH(CO_2Et)\cdot CHMe\cdot CO_2Et$, to *aγ-dimethylparaconic acid*, $\begin{matrix} O\text{—}CHMe \\ | \\ CO\cdot CHMe \end{matrix}\!\!>\!CH\cdot CO_2H$, crystallising from water in slender needles or from ether in large, transparent prisms, melting at 131° and boiling at 195° under 14 mm. pressure. The *silver* salt forms slender needles. The *ethyl* ester forms a colourless liquid boiling at 142° under 14 mm. pressure, and has a sp. gr. 1·101 at 15°.

aγ-Dimethylparaconic acid decomposes when slowly distilled, yielding methylethylmaleic acid (Fittig and Parker, Abstr., 1892, 814) and a-methyl-Δ^{β}-pentenoic acid, which are separated by crystallisation of their barium salts.

Methylethylmaleic anilide, $C_{12}H_{13}O_2N$, is a viscous liquid, boiling at 184° under 14 mm. pressure. Sodium hydroxide decomposes methylethylmaleic acid, forming methylethylfumaric and aγ-dimethylitaconic acids. *Methylethylfumaric acid*, $CO_2H\cdot CEt{:}CMe\cdot CO_2H$, forms small, granular crystals and melts at 202°. The *barium* and *calcium* salts form slender needles. *aγ-Dimethylitaconic acid*,

$$CHMe{:}C(CO_2H)\cdot CHMe\cdot CO_2H,$$

forms prismatic crystals and melts and decomposes at 148—150°.

a-Methyl-Δ^{β}-pentenoic acid, $CHMe{:}CH\cdot CHMe\cdot CO_2H$, forms a colourless liquid boiling at 198—199° under 740 mm. pressure, and has a sp. gr. 0·966 at 15° and $n_D = 1{\cdot}44020$. The *calcium* salt forms slender needles. Boiling with sodium hydroxide converts the acid into methylethylacrylic acid (Lieben and Zeisel, Abstr., 1883, 571).

C. H. D.

Action of Potassium Carbonate on *iso*Butaldehyde. Felix M. A. Kirchbaum (*Monatsh.*, 1904, **25**, 249—266. Compare Brauchbar, Abstr., 1897, i, 137; 1898, i, 353).—Contrary to Brauchbar's statement, di*iso*butaldehyde is obtained along with octoglycol *iso*butyrate, and not alone, when *iso*butaldehyde is allowed to remain in contact with an equal volume of a saturated aqueous solution of potassium carbonate. The yield of di*iso*butaldehyde decreases with the use of anhydrous potassium carbonate or with an increase in the temperature of reaction. The best yield (86·66 per cent.) of octoglycol *iso*butyrate is obtained by the action of anhydrous

potassium carbonate at 65°, under which conditions no di*iso*butaldehyde is present after 60 hours. With 50 per cent. aqueous potassium carbonate, small amounts of products boiling below 100° under 17 mm. pressure, and, if the reaction is carried out at 125—130°, also products boiling above 138° under 17 mm. pressure are formed.

Octoglycol *iso*butyrate cannot be obtained free from di*iso*butaldehyde by fractional distillation under 17 mm. pressure, but must be distilled at 250° under atmospheric pressure, at which temperature di*iso*butaldehyde is decomposed. Di*iso*butaldehyde remains liquid after several months; Brauchbar's crystals melting at 90—92° could not be obtained. G. Y.

Methyl Ether of Acetylcarbinol, $COMe\cdot CH_2\cdot OMe$. Louis Henry (*Compt. rend.*, 1904, 138, 970—972).—The crystalline compound melting at 131° and boiling at 196°, which occurs as a secondary product in the preparation of acetylcarbinol (acetol) by the action of methyl alcohol on pyruvyl formate (compare Abstr., 1902, i, 736), and shown by Kling (compare following abstract) to be a polymeride of acetylcarbinyl methyl ether, has different physical and chemical properties (1) from the normal compound, which is a liquid boiling at 118°, having a sp. gr. 0·9570 at 20°, and reducing Fehling's solution (compare Abstr., 1881, 1121. Compare also Leonardi and de Franchis, Abstr., 1903, i, 787); (2) from the isomeric *methyl glycide*, $OMe\cdot CH_2\cdot CH<\overset{CH_2}{\underset{O}{|}}$, which boils at 118° and does not reduce Fehling's solution. M. A. W.

Methyl Acetolate. André Kling (*Compt. rend.*, 1904, 138, 972—975).—The polymeride of methyl acetolate (α-methoxy-β-ketopropane), obtained by Henry by the action of methyl alcohol on pyruvyl formate (compare Henry, Abstr., 1902, i, 736, and preceding abstract), also prepared by the direct action of methyl alcohol on acetylcarbinol at a temperature of 140°, is a crystalline compound which sublimes in long needles when heated and melts at 131°, is slightly soluble in water (1 part in 100) or methyl alcohol (4 parts in 100) or benzene, much more soluble in chloroform (20 parts in 100 at 15°). It does not reduce Fehling's solution, is not decomposed by boiling alkalis, does not react with phenylhydrazine acetate in the cold, but on warming forms the osazone of acetylcarbinol melting at 145°; is slowly attacked by boiling acid anhydrides to form methyl alcohol and the corresponding ethereal salt of acetylcarbinol; it is readily hydrolysed by dilute acids regenerating acetylcarbinol, slowly hydrolysed by water, and not attacked by the diastases (invertase, maltase emulsin, saline). The molecular weight, determined by the depression of the freezing point of benzene or ethylene bromide, shows that the substance is bimolecular, and the constitutional formula $O<\begin{matrix}CMe(OMe)\cdot CH_2\\CMe(OMe)\cdot CH_2\end{matrix}>O$ is suggested by the author. M. A. W.

Action of Hydrogen Peroxide on 1 : 2-Diketones and on α-Ketonic Acids. Arnold F. Holleman (*Proc. k. Akad. Wetensch. Amsterdam,* 1904, 6, 715).—Aqueous solutions of pyruvic acid,

benzoylformic acid, and thienylglyoxylic acid, when heated with the calculated amount of 30 per cent. hydrogen peroxide, were oxidised to acetic, benzoic, and thiophenic acids respectively.

Benzil, camphorquinone, and phenanthraquinone were also oxidised when dissolved in glacial acetic acid and then warmed for some days with a small excess of hydrogen peroxide, according to the general scheme, $R \cdot CO \cdot CO \cdot R' + HO_2H = R \cdot CO_2H + R' \cdot CO_2H$; camphorquinone first formed the anhydride, which was converted by boiling with dilute alkali into camphoric acid. A. McK.

Action of Calcium Hydroxide on *l*-Arabinose. Heinrich Kiliani and F. Koehler (*Ber.*, 1904, **37**, 1210—1215).—Details are given for preparing *l*-arabinose on the large scale from cherry-gum and for purifying the product. On agitating *l*-arabinose (1 part) during 14 days with water (10 parts) to which quicklime (0·2 part) had been added, and, after removing the lime with oxalic acid, extracting with ether, a considerable quantity of lactic acid was obtained, which was identified by means of its zinc salt; on dividing the insoluble residue into a number of fractions by dissolving in alcohol and precipitating with absolute ether, only syrups could be obtained which showed no tendency to crystallise and from which no definite hydrazide, hydrazone, or benzoate could be prepared. The original calcium salt was then fractionally precipitated with alcohol and the various fractions analysed; the numbers for the first two fractions agreed approximately with the formula $(C_5H_9O_5)_2Ca$; the later fractions having the composition $(C_6H_{11}O_6)_2Ca$. It thus appears that the acids formed contained carbon and oxygen in the ratio $C : O = 1 : 1$, as in the saccharic acids, and that from a C_5 sugar a C_6 acid had been synthesised. W. A. D.

Crystallised Melibiose. Arminius Bau (*Zeit. Ver. deut. Zucker-Ind.*, 1904, **579**, 481—521. Compare Abstr., 1902, i, 347).—Melibiose crystallises in the monoclinic system [$a : b : c$ = 1·92275 : 1 : 2·01243; $\beta = 77°16'$]. The hydrated sugar has $[\alpha]_D$ + 129·641°, the value for anhydrous melibiose being + 143·27°. It is hydrolysed by dilute hydrochloric, sulphuric, or oxalic acid, but not by lactic, citric, or tartaric acid; on long heating with the three last named organic acids, melibiose undergoes a diminution in its rotatory power, probably owing to the formation of esters of the acids. The actions of enzymes, at different temperatures, on melibiose were examined, and also the fermentation of the sugar by yeasts of various types. The copper reducing power was measured by boiling 50 c.c. of Fehling's solution in a porcelain beaker, adding 25 c.c. of the melibiose solution, and boiling for a further 4 minutes; if x is the amount of copper obtained, y_1 and y_2 the corresponding quantities of crystallised and anhydrous melibiose respectively, then:

$$y_1 = -\ 0·0008 + 0·9731\,x + 0·310552\,x^2; \text{ and}$$
$$y_2 = -\ 0·0007 + 0·88\,x + 0·2834\,x^2.$$

The means for detecting and estimating melibiose are described, and also its separation from other sugars and from starch conversion products. T. H. P.

Nitrocelluloses. II. Carl Haeussermann (*Ber.*, 1904, 37, 1624—1625. Compare this vol., i, 144).—The volatile product obtained on distilling nitrocellulose with alkali hydroxides may be distilled under reduced pressure, and is then obtained as a colourless, mobile oil, dissolving readily in water and boiling at 60—80° under atmospheric pressure. It readily yields iodoform, but does not reduce ammoniacal silver nitrate. Similar products are obtained from amorphous nitrocellulose, nitroamyloid, and the nitro-compounds of inulin, starch, lactose, and dextrose. C. H. D.

Purification of Leucine and Tyrosine by E. Fischer's Method of Esterisation. (*Trans. Guinness Res. Lab.*, 1903, 1, 57—60).—Leucine and tyrosine have been purified by the method proposed by Fischer (Abstr., 1901, i, 192) for separating the monoamino-acids resulting from the hydrolysis of a proteid, consisting in esterifying the crude mixture of amino-acids by means of hydrochloric acid and alcohol, separating the free esters from their hydrochlorides by the action of concentrated alkali hydroxide solution at a low temperature, fractionally distilling the esters under 9—10 mm. pressure, and hydrolysing those fractions distilling below 85° by boiling for some hours with water in a reflux apparatus.

The leucine employed was a well-crystallised product prepared by Kahlbaum by the hydrolysis of the cervical ligament with acid, and gave the following results on examination: nitrogen (Kjeldahl's method), 10·3 (required 10·7) per cent.; nitrogen (Sachsse-Kormann method, nitrous acid), 6·8 (required 10·7) per cent.; $[\alpha]_D$ of 5 per cent. solution in 20 per cent. hydrochloric acid, +8·1° (required 17·6°). After purification of the leucine as above, it gave the following results: $[\alpha]_D$ + 6·1°, this small number being probably due to partial racemisation; melting point on quickly heating, 280°; Cohn (Abstr., 1895, ii, 25) observed 250° for an optically active leucine prepared by the pancreatic digestion of blood fibrin. Estimations of the nitrogen by the Sachsse-Kormann process gave 97·6, 101·1, and 100·0 per cent. of the theoretical amount; copper in the copper salt, 19·58 (required 19·64) per cent.

A sample of tyrosine obtained by the acid hydrolysis of horn-shavings gave, after purification: $[\alpha]_D$ in 17·5 per cent. hydrogen chloride solution, −8·17° (Fischer gave −8·6°); temperature of melting and decomposition, 287° (Lippmann gave about 235° and Fischer 310—314° for rapid heating); nitrogen by Kjeldahl's process, 7·65 (required 7·75) per cent. Another specimen of tyrosine, prepared by "chemolysis" of the albumin of ox-brain, was purified by dissolving in hydrochloric acid and precipitating by ammonia, after which it gave 7·70 per cent. of nitrogen by Kjeldahl's method; $[\alpha]_D$ in 20 per cent. hydrogen chloride solution, −2·92°; melting point, 360°; copper in copper salt, 14·50 (required 14·9) per cent. This specimen was found to be much less soluble in 20 per cent. hydrogen chloride solution than that prepared from horn-shavings, and is doubtless partially racemised. T. H. P.

The Spontaneous Decomposition of Glycine Ethyl Ester. THEODOR CURTIUS (*Ber.*, 1904, 37, 1284—1300).—Glycine ethyl ester decomposes spontaneously, forming glycine anhydride and the so-called "biuret base" (Curtius, Abstr., 1883, 337). The latter was described by Schwarzschild (Abstr., 1903, i, 780) as containing an open chain of seven glycine groups, but is now shown to contain only four such groups.

Ethyl aminoacetyldiglycylaminoacetate,

$$NH_2·CH_2·CO[NH·CH_2·CO]_2·NH·CH_2·CO_2Et,$$

is best prepared by mixing pure ethyl glycine with absolute ether, air being excluded. The decomposition takes place very slowly, and pure biuret base is obtained. With impure ester, or in presence of moisture, the product contains considerable quantities of glycine anhydride, apparently in combination with the base. The ester crystallises from water in small tablets, sinters at 218°, and decomposes without melting at 270°. It is readily soluble in water, sparingly so in hot chloroform or ethyl acetate, almost insoluble in alcohol, ether, or benzene. Solutions of metallic salts give a large number of reactions characetristic of proteids. The *picrate* crystallises in long prisms and melts at 189°. The *hydrochloride* forms small tablets and melts and decomposes at 192—193°. The *platinichloride* forms bright orange tablets, containing $2H_2O$, and melts and decomposes at 112°. The *copper* salt,

$$(C_8H_{13}O_5N_4)_2Cu,H_2O,$$

crystallises in bright blue tablets, becoming anhydrous and colourless at 110° and melting at 158—159° to a red liquid. The bright blue aqueous solution becomes red on addition of alkalis, and is decolorised by acids.

Ethyl diazoacetyldiglycylaminoacetate,

$$N_2\!:\!CH·CO·[NH·CH_2·CO]_2·NH·CH_2·CO_2Et,$$

forms bright yellow tablets and becomes more intensely yellow at 130°, and melts and decomposes at 159°. Ammonia forms *diazoacetyldiglycylglycinamide*, crystallising in yellow tablets, blackening at 200°, and melting and decomposing at 240°. Iodine converts the diazo-ester into *ethyl di-iodoacetyldiglycylaminoacetate*, a white precipitate, sintering at 160° and melting and decomposing at 190°. Boiling the diazo-ester with water yields *ethyl hydroxyacetyldiglycylaminoacetate*, which forms slightly yellow crystals.

Hydrazine hydrate and the biuret base form *aminoacetyldiglycylglycinehydrazide*, $NH_2·CH_2·CO·[NH·CH_2·CO]_2·NH·CH_2·CO·NH·NH_2$, a white powder, not melted at 300°. The *hydrochloride* forms a colourless, highly hygroscopic mass, and decomposes at 112°. Sodium nitrite forms a colourless compound melting and decomposing at 79—80°, which is probably the *hydroxyazoimide*,

$$OH·CH_2·CO·[NH·CH_2·CO]_2·NH·CH_2·CO·N_3.$$

Benzaldehyde condenses with the hydrazide to form *benzylideneaminoacetyldiglycylglycinebenzylidenehydrazine*,

$$CHPh\!:\!N·CH_2·CO·[NH·CH_2·CO]_2·NH·CH_2·CO·NH·N\!:\!CHPh,$$

melting at 228°.

Hippurazide condenses with the biuret base to form *ethyl benzoyltetraglycylaminoacetate*, $COPh·[NH·CH_2·CO]_4·NH·CH_2·CO_2Et$, which

darkens at 240° and melts and decomposes at 256—257°. The *hydrazide* melts at 272—274° and its *benzylidene* derivative at 275°.

When the biuret base is heated for several hours at 100° in a vacuum, *octoglycine anhydride*, $(NH\cdot CH_2\cdot CO)_8$, is obtained as an infusible substance which gives the biuret reaction. C. H. D.

Complex Compounds of Succinimide. LEO TSCHUGAEFF (*Ber.*, 1904, 37, 1479—1481).—When aqueous ammonia is cautiously added to a concentrated alcoholic solution of copper chloride and succinimide, a compound, $\left(\begin{matrix}CH_2\cdot CO\\ | \\ CH_2\cdot CO\end{matrix}\!\!>\!N\right)_2Cu,2NH_3$, is formed, crystallising in copper-red needles. With primary amines, similar compounds are formed; thus, the *allylamine* compound crystallises in long, silky, copper-red needles with a metallic lustre and the *benzylamine* derivative is similar. In aqueous solution, using a smaller quantity of ammonia, a compound of the type $\left(\begin{matrix}CH_2\cdot CO\\ | \\ CH_2\cdot CO\end{matrix}\!\!>\!N\right)_2Cu,NH_3,3H_2O$ is formed, crystallising in dark blue, prismatic needles; the *methylamine* derivative forms similar violet crystals. E. F. A.

Preparation of Substituted Succinimides in Aqueous Solution. GUSTAV KOLLER (*Ber.*, 1904, 37, 1598—1599).—Substituted succinimides have hitherto been prepared by heating succinic acid with bases and distilling off the water formed. A more convenient method, yielding very pure products, is that of boiling succinic anhydride and primary amines suspended in water. The preparation of phenylsuccinimide, *p*-tolylsuccinimide, and β-naphthylsuccinimide is described. C. H. D.

Formation of Uroxanic Acid and of Allantoin from Uric Acid. ERNST E. SUNDVIK (*Zeit. physiol. Chem.*, 1904, 41, 343—347. Compare Claus, *Ber.*, 1874, 7, 227, and Abstr., 1895, i, 129).—A quantitative yield of allantoin may be obtained by oxidising uric acid with alkaline permanganate according to the method previously described for the preparation of uroxanic acid, except that the filtrate is immediately acidified with acetic acid.

It is suggested that an intermediate product,

$$CO\!<\!\begin{matrix}NH\cdot CO\cdot C(OH)\cdot NH\\ \qquad\qquad | \\ NH\text{——}C(OH)\cdot NH\end{matrix}\!>\!CO,$$

is formed by the oxidation of uric acid, and that under the influence of alkali this is transformed into uroxanic acid,

$$\begin{matrix}CO_2H\cdot C(OH)\cdot NH\\ | \\ NH_2\cdot CO\cdot NH\cdot C(OH)\cdot NH\end{matrix}\!>\!CO,$$

but in the presence of acids into allantoin. J. J. S.

Preparation of Alkali Cyanides. DEUTSCHE GOLD- & SILBER-SCHEIDE-ANSTALT VORM. ROESSLER (D.R.-P. 149678. Compare this vol., i, 380).—Not only solid carbon, but also a great variety of volatile organic compounds, react with fused sodamide to form disodium cyan-

amide. Fused sodium or a lead-sodium alloy is heated at 400° and a current of mixed ammonia and acetylene in equivalent proportions is led in, the temperature being gradually raised to 550°. No sodium carbide is formed. When the whole is converted into disodium cyanamide, the temperature is raised to 750—800°, and carbon or acetylene added in sufficient quantity to form sodium cyanide. C. H. D.

Complex Cyano-copper-ammonia Compounds. FREDERICK P. TREADWELL and CONWAY VON GIRSEWALD (*Zeit. anorg. Chem.*, 1904, 39, 84—97).—Many of the complex cyano-copper-ammonia compounds described in the literature as uniform substances are not so. The compound $Cu_2(CN)_2,2NH_3$, best prepared by boiling cuprous cyanide with aqueous ammonia in the absence of air or by boiling the potassium cuprocyanides with water in the absence of air and then passing a current of ammonia until the cuprous cyanide, which separates at first, is redissolved, forms colourless crystals and is identical with the compound described by Malmberg. It is converted by boiling water into ammonia and cuprous cyanide. Its ammoniacal solution quickly assumes a deep blue tint on exposure to the atmosphere; blue needles separate after a time, and these in turn are converted into a green compound. When the potassium cuprocyanide of the composition $[Cu_2(CN)_3,H_2O]K$ is treated with dry ammonia, it is converted into a *compound* of the probable composition $[Cu_2(CN)_3,NH_3]K$, whilst the other potassium cuprocyanides, $[Cu_2(CN)_4]K_2$ and $[Cu_2(CN)_8]K_6$, are not acted on by ammonia.

Ammonium cuprocyanide, $[Cu_2(CN_3),H_2O]NH_4$, prepared from a mixture of freshly-precipitated cuprous cyanide and aqueous hydrocyanic acid by the action of ammonia, forms colourless, glassy, triclinic crystals. It parts with water at about 100°; at about 120°, ammonium cyanide is produced, and finally metallic copper separates. When heated with ammonia in the absence of air, it forms the compound $[Cu_2(CN)_2(NH_3)_2]$.

The *compound* $[Cu_2(CN)_3(NH_3)]_2Cu$, prepared from the ammonium salt, $[Cu_2(CN)_3,NH_3],NH_4$, by double decomposition with cupric acetate, forms a brown, amorphous powder.

The *salt* $[Cu_2(CN)_3(NH_3)_2]_2Cu$, best prepared by boiling the compound $[Cu_2(CN)_3,H_2O]NH_4$ with ammonia, crystallises in violet, rhombic leaflets; it is also formed by prolonged boiling of the compound $Cu_2(CN)_4(NH_3)_4Cu$, which separates in blue needles when potassium cuprocyanide interacts with ammonia. The *salt*

$$[Cu_2(CN)_4(NH_3)_3]Cu,$$

prepared by passing hydrogen cyanide into an ammoniacal solution of cupric oxide, forms glistening, green, rhombic needles. When acted on by mineral acids, hydrogen cyanide and cupric cyanide are formed; at 120°, it evolves ammonia. When alcohol is added to its concentrated ammoniacal solution, the *salt* $[Cu_2(CN)_4(NH_3)_4]Cu$ is precipitated; it forms long, blue needles, which readily part with ammonia to form the green salt. A. McK.

Electrolysis of Potassium Double Cyanides. H. VON HAYEK (*Zeit. anorg. Chem.*, 1904, 39, 240—256).—The electrolytic oxidation

of potassium ferrocyanide was examined with the view of ascertaining the experimental conditions under which complex oxidation occurs, and of finding the influence of concentration on the current yield and current density. The liquid at the anode should be kept in constant motion by a stirrer, and should be kept alkaline in order to prevent the formation of free hydroferrocyanic acid. The space occupied by the anode should be twice as great as that occupied by the cathode. The rotating anode should present as large a surface as possible. The electrodes were made of nickel. The potassium ferrocyanide and ferricyanide were estimated by the methods of de Haen and Gintl. A current yield of 100 per cent. can be attained. The concentration of the electrolyte exercises, within very wide limits, no influence on the yield. The limit to which the concentration of the total electrolyte may be lessened increases with increasing original concentration; the limit to which the concentration of the solution at the anode may be diminished is independent of the original concentration and of the amount of potassium ferricyanide formed. With regard to the influence of the current density on the current yield, it was found that if a definite limit of the current density were exceeded whilst the concentration was constant, secondary processes set in, and their intensity increased rapidly, whilst the current yield sank to a corresponding degree. The maximum value of the current density which may be employed increases with increase of concentration. The secondary processes mentioned are: (1) the decomposition of water by the anion $Fe(CN)_6$, whereby free alkali at the anode will be neutralised, (2) the electrolytic decomposition of the potassium ferrocyanide formed, and (3) the electrolytic decomposition of the potassium hydroxide present.

When potassium manganicyanide, $K_3Mn(CN)_6$, is electrolysed, the solution is first dissociated into the ions K_3 and $Mn(CN)_6$. The final product of the cathodic reduction is manganous hydroxide. The stability of the anion $Mn(CN)_6$ is distinctly less than that of the ion $Fe(CN)_6$.

Potassium nickel cyanide, $K_2Ni(CN)_4$, undergoes electrolytic dissociation into the ions K and $Ni(CN)_4$. The final product of the cathodic reduction was a substance which was not isolated owing to its instability, but which, on exposure to the atmosphere, was rapidly converted into the original double cyanide. The stability of the anion $Ni(CN)_4$ is slight; it splits up readily into $Ni(CN)_2$ and $(CN)_2$.

Potassium cobalticyanide, $K_3Co(CN)_6$, undergoes electrolytic dissociation into the ions K_3 and $Co(CN)_6$. The final product at the anode is the oxide, Co_2O_3. The stability of the anion $Co(CN)_6$ is slight. The oxidation at the anode was more marked in this case than with the other compounds examined, since oxides of nitrogen and ozone were produced. A. McK.

Preparation of Platinocyanides. ANDRÉ BROCHET and JOSEPH PETIT (*Compt. rend.*, 1904, 138, 1095—1097).—See this vol., ii, 414.

Condensation Products of Cyanoacetic Esters with Acylcyanoacetic Esters. CH. SCHMITT (*Bull. Soc. chim.*, 1904, 31, 529—530. Compare Abstr., 1903, i, 398).—When an excess of

methyl cyanoacetate is employed in preparing methyl benzoylcyanoacetate by Haller's process, and especially when the reaction product is heated on the water-bath after the whole of the alcohol has been driven off, there is formed a *substance* $C_{15}H_{14}O_5N_2$, which crystallises from alcohol, melts at 162°, is insoluble in water or ether, and is hydrolysed by potassium hydroxide dissolved in alcohol, into methyl cyanoacetate, methyl benzoylcyanoacetate, and benzoic acid. It gives no coloration with ferric chloride, but is coloured yellow by alkalis, belongs to the series of compounds investigated by Guinchant (Abstr., 1896, i, 594), and probably has the constitution

$$HO\cdot CPh[CH\cdot(CN)\cdot CO_2Me]_2.$$

From acetyl chloride and methyl cyanoacetate under the same conditions, the *substance* $C_{16}H_{19}O_8N_3$, is obtained; this is slightly soluble in alcohol, acetone, and chloroform, and insoluble in other solvents. When hydrolysed with potassium hydroxide dissolved in alcohol, there are formed methyl cyanoacetate, acetic acid, and an *acid*, $C_{12}H_{14}O_8N_2$, which melts at 158—160°. T. A. H.

Diazo-fatty Esters. THEODOR CURTIUS and E. MÜLLER (*Ber.* 1904, 37, 1261—1279).—Very few diazo-fatty esters have hitherto been prepared in a pure state (compare Curtius and Koch, Abstr., 1889, 376). Only esters of α-amino-acids yield diazo-esters; β- and γ-amino-esters, on the other hand, do not form diazo-compounds, and an $\alpha\beta$-diamino-ester therefore yields an α-diazo-β-hydroxy-ester. It is not possible to purify the diazo-esters by fractional distillation, but the method of distillation with steam from an excess of barium hydroxide may be employed with success (Abstr., 1884, 42). From a comparison of the fatty diazo-compounds, the rule is deduced that only fatty compounds in which the amino-group, carbonyl, and at least one hydrogen atom are attached to the same carbon atom yield diazo-compounds with nitrous acid.

Ethyl diazosuccinate, $CO_2Et\cdot C(N_2)\cdot CH_2\cdot CO_2Et$, remains on evaporating its dry ethereal solution in a vacuum as a yellow oil, which has a sp. gr. 1·132 at 18°/4° and n_D 1·4615 at 18°, and decomposes violently at 120° under 10 mm. pressure (compare Curtius and Lang, Abstr., 1892, i, 451).

Ethyl phenylalanine hydrochloride, $CH_2Ph\cdot CH(NH_2)\cdot CO_2Et,HCl$, melts at 127° and reacts with sodium nitrite to form *ethyl phenylalanine nitrite*, $CH_2Ph\cdot CH(NH_2)\cdot CO_2Et,HNO_2$, an unstable, white, crystalline mass (compare ethyl glycine nitrite, Abstr., 1888, 576). In presence of dilute sulphuric acid, *ethyl α-diazo-β-phenylpropionate*, $CH_2Ph\cdot C(N_2)\cdot CO_2Et$, is formed, and is obtained after distillation from barium hydroxide as a golden-yellow oil with aromatic odour, becoming viscous in liquid air and boiling undecomposed at 90—94° under 11 mm. pressure. It has a sp. gr. 1·107 at 20°/4° and n_D 1·5367 at 16°. Dilute mineral acids decompose it only on warming. The crude ester is partially converted on distillation into *ethyl α-hydroxy-β-phenylpropionate*, $CH_2Ph\cdot CH(OH)\cdot CO_2Et$, a colourless oil boiling at 126° under 15 mm. pressure.

Methyl phenylalanine, $CH_2Ph\cdot CH(NH_2)\cdot CO_2Me$, is a colourless liquid, which boils at 141° under 12 mm. pressure, and has a sp. gr. 1·096

at 22°/4° and n_D 1·5203 at 20°. The *hydrochloride* forms yellow needles and melts and decomposes at 158°. *Methyl a-diazo-β-phenylpropionate* boils at 85—87° under 12 mm. pressure and is less stable towards acids than the ethyl ester. It has a sp. gr. 1·126 at 20°/4° and n_D 1·5435 at 26°.

Ethyl a-diazopropionate, N_2:CMe·CO_2Et, from ethyl alanine, is a yellow oil, readily decomposed by acids. It boils at 65—68° under 41 mm. pressure, solidifies to a crystalline mass in solid carbon dioxide and ether, and has a sp. gr. 1·086 at 12°/4° and n_D 1·4472 at 18°. The methyl ester is similar, and boils at 43—45° under 11 mm. pressure, and has a sp. gr. 1·101 at 13°/4° and n_D 1·4487 at 20°. Both esters partially decompose on distillation, forming esters of dimethylfumaric acid.

Ethyl a-aminobutyrate hydrochloride, CH_2Et·CH(NH_2)·CO_2Et,HCl, from a aminobutyric acid, melts at 130·5° and forms *ethyl a-diazobutyrate*, CH_2Et·C(N_2)·CO_2Et, a yellow oil which boils at 63—65° under 11 mm. pressure and has a sp. gr. 1·028 at 21°/4° and n_D 1·4460 at 21°.

Methyl a-aminobutyrate hydrochloride melts at 139°. *Methyl a-diazobutyrate* is an orange-yellow oil, which boils at 54—56° under 12 mm. pressure and has a sp. gr 1·043 at 18°/4° and n_D 1·4465 at 24°.

Ethyl a-diazohexoate, CH_2Pr·C(N_2)·CO_2Et, from ethyl leucine hydrochloride (E. Fischer, Abstr., 1901, i, 192), forms a yellow oil, which boils at 70—73° under 12 mm. pressure and crystallises in liquid air. It has a sp. gr. 0·9605 at 15°/4° and n_D 1·4329 at 19°. Iodine and ammonia convert it into *di-iodohexoamide*, CH_2Pr·CI_2·CO·NH_2, which crystallises from water in small, bright yellow, sparingly soluble needles and darkens at 180°, decomposing and evolving iodine at higher temperatures.

Ethyl β-aminopropionate, from β-alanine, reacts with nitrous acid in the presence of hydrochloric acid to form ethyl β-hydroxypropionate, together with a small quantity of ethyl β-chloropropionate. In similar manner, ethyl β- and γ-aminobutyrates yield ethyl β- and γ-hydroxybutyrates respectively.

Ethyl β-amino-a-hydroxypropionate yields ethyl aβ-dihydroxypropionate. Ethyl hexahydroanthranilate (Einhorn and Meyenberg, Abstr., 1894, i, 591) yields ethyl hexahydrosalicylate.

Ethyl aβ-diaminopropionate hydrochloride,

NH_2·CH_2·CH(NH_2)·CO_2Et,2HCl,

from hippurylaspartic acid, melts and decomposes at 142—144° and reacts with sodium nitrite to form *ethyl a-diazo-β-hydroxypropionate*, OH·CH_2·C(N_2)·CO_2Et, a yellow oil.

Diazo-compounds could not be obtained from the ethyl esters of tyrosine or phenylglycine. C. H. D.

Cacodylic Acid and Amphoteric Substances. PAUL THIEBAUT MULLER and ED. BAUER (*Compt. rend.*, 1904, 138, 1099—1100).—Zawidzki's conclusion that cacodylic acid is a pseudo-acid (compare Abstr., 1903, i, 801 ; this vol., i, 232) is not supported by the physicochemical properties of the acid (compare Hantzsch, this vol., i, 381), also the molecular refraction for the D ray of *N*/4 cacodylic acid at 20° is 23·95, whilst that of its sodium salt under the same conditions is 25·53 ; the difference, 1·58, between these two values is

characteristic of weak carboxylic acids and points to the acid and the salt having the same constitution (compare Abstr., 1903, i, 77, 78; ii, 705); further, the heat of neutralisation of cacodylic acid is 14·11 Cal. (compare Imbert, Abstr., 1900, i, 145), and hence its heat of dissociation is +0·4 Cal., equal to that of acetic acid but of opposite sign, and the temperature coefficient of the affinity constant K of cacodylic acid is therefore not abnormal. M. A. W.

Synthesis of Benzene Hydrocarbons by Reduction of Oxygenated Groups. AUGUST KLAGES and CH. STAMM (*Ber.*, 1904, 37, 1715—1721).—*iso*Durenesulphonic acid, prepared from *iso*durene by the action of fuming sulphuric acid, crystallises in glistening leaflets, melts at 79—80°, and is decomposed with formation of *iso*durene when heated at 100° with phosphoric acid. Dibromo*iso*durene melts at 199°; when heated at 180—200° with hydriodic acid, it is converted into mesitylene, which is also formed when *iso*durene is heated with hydriodic acid and red phosphorus at 180—200°. Ethylmesitylene is obtained by reduction of vinylmesitylene with sodium and alcohol, or of ethyl mesitylcarbinol with hydriodic acid. The sulphonic acid is decomposed by phosphoric acid at 100°. Dibromoethylmesitylene melts at 59—60°, not at 219° (Thöl and Tripke, *Ber.*, 1895, 28, 2462), and yields mesitylene when heated with hydriodic acid at 200°.

Propylmesitylene is obtained by the reduction of mesitylethylcarbinol with hydriodic acid and red phosphorus. The sulphonic acid is decomposed by phosphoric acid at 100°. Propylmesitylene yields mesitylene when heated with hydriodic acid at 250—260°. iso*Butylmesitylene*, $C_6H_2Me_3\cdot CH_2Pr^{\beta}$, is prepared by reducing mesityl*iso*propyl carbinol; it is a colourless oil, which boils at 125—127° under 24 mm., at 228—230° under 745 mm. pressure, has a sp. gr. 0·8782 at 18°/4°, and n_D 1·5004 at 13°. It remains unchanged when heated with hydriodic acid at 200°. The *sulphonic acid* is decomposed by phosphoric acid at 100°.

iso*Pentylmesitylene* boils at 133—135° under 19 mm., at 241—243° under 747 mm. pressure, has a sp. gr. 0·8751 at 23°/4°, n_D 1·4976 at 23°, and is only slightly decomposed by hydriodic acid at 200°. The *sulphonic acid* is an oil, soluble in water. With bromine in aqueous solution, it yields *dibromo*iso*pentylmesitylene*, which crystallises in colourless needles and melts at 44°.

Heptylmesitylene is a colourless oil, which boils at 157—158° under 15 mm., at 271—272° under 750 mm. pressure, has a sp. gr. 0·8753 at 17°/4° and n_D 1·4970 at 17°, and is not acted upon by hydriodic acid at 250°. The *sulphonic acid* yields a *magnesium* salt $C_{32}H_{50}O_6S_2Mg$, which crystallises in small leaflets. G. Y.

Derivatives of *m*-Di-iodobenzene with Polyvalent Iodine. CONRAD WILLGERODT and A. DESAGA (*Ber.*, 1904, 37, 1301—1310. Compare Abstr., 1903, i, 743, 745, 746).—A solution of *m*-di-iodobenzene in chloroform absorbs chlorine, forming m-*iodophenyl iododichloride*, $C_6H_4I\cdot ICl_2$, which crystallises in slender, yellow needles, decomposes at 112°, and dissolves in organic solvents. The further action of chlorine produces yellow, silvery leaflets of m-*phenylene*

di-iodotetrachloride, $C_6H_4(ICl_2)_2$, decomposing at 122° and dissolving readily in benzene or acetone, sparingly in ether, chloroform, or acetic acid.

m-*Iodoiodosobenzene*, $C_6H_4I{\cdot}IO$, forms a bright yellow, amorphous powder, insoluble in organic solvents, and explodes on heating at temperatures varying with the rapidity of heating. Dry hydrogen chloride or phosphorus pentachloride converts it into the chloride. Glacial acetic acid forms transparent needles of m-*iodophenyl iododiacetate*, $C_6H_4I{\cdot}I(OAc)_2$, melting at 160°. The *basic sulphate*, $[C_6H_4I{\cdot}I(OH)]_2SO_4$, decomposes at 108°. The *basic nitrate* was only obtained in an impure state. The *basic chromate* is a red, amorphous precipitate.

m-*Di-iodosobenzene*, $C_6H_4(IO)_2$, forms a bright yellow, amorphous powder, insoluble in all solvents, and explodes at 108°. Acetic acid forms m-*phenylene di-iodotetra acetate*, $C_6H_4[I(OAc)_2]_2$, a snow-white powder melting at 204°. The reddish-yellow *chromate* is unstable and explodes at 60°.

m-*Iodoiodoxybenzene*, $C_6H_4I{\cdot}IO_2$, crystallises from boiling water in colourless needles and explodes violently at 216—218°. m-*Di-iodoxybenzene*, $C_6H_4(IO_2)_2$, forms white, microscopic tablets and explodes violently at 261°, and also on percussion.

Phenyl-m-*iodophenyliodinium hydroxide*, $C_6H_4I{\cdot}IPh{\cdot}OH$, from *m*-iodoiodosobenzene and iodoxybenzene with silver oxide, is obtained as a strongly alkaline solution in water. The *chloride* crystallises in white, readily soluble needles and melts at 134°, the sparingly soluble *bromide* forms small leaflets and melts at 169°, the insoluble yellow *iodide* decomposes at 89°. The *periodide*, $C_6H_4I{\cdot}IPh{\cdot}I_3$, forms small, reddish-brown needles and melts at 118°. The *dichromate* forms an orange precipitate and decomposes at 135°, the colourless, amorphous *mercurichloride* melts at 56°, and the amorphous, flesh-coloured *platinichloride* melts at 187°.

Di-m-*iodophenyliodinium hydroxide*, $I(C_6H_4I)_2{\cdot}OH$, has only been obtained in solution. The *chloride* crystallises from benzene in small needles and melts at 156°, the *bromide* forms an amorphous powder and decomposes at 163°, the yellow *iodide* melts at 141°, the reddish-yellow *dichromate* darkens at 85°, and the *platinichloride* darkens at 109° and melts at 191°.

Iodophenyldi-m-*iodophenyliodinium hydroxide*, $C_6H_4I{\cdot}I(C_6H_3I_2){\cdot}OH$, from *m*-iodoiodosobenzene, is obtained in solution. The *bromide* forms a yellow, amorphous precipitate and melts at 109°, the *iodide* forms a chestnut-brown precipitate and blackens at 52°, the *dichromate* is red and decomposes at 91°, the *platinichloride* is flesh-coloured, and sinters at 120° and melts at 171°.

Dichloroethyl-m-*iodophenyliodinium chloride*, $C_2H_3Cl_2{\cdot}ICl{\cdot}C_6H_4I$, prepared from *m*-iodophenyl iodochloride and silver acetylide-silver chloride, crystallises from water in white needles and melts at 148°.

Di-m-*iodophenyl*-m-*phenylenedi-iodinium hydroxide*,

$$C_6H_4[I(OH){\cdot}C_6H_4I]_2,$$

is obtained in the form of a strongly alkaline solution. The *bromide* sinters at 58° and melts at 146°, the pale yellow, unstable *iodide* decomposes at 140°, the *platinichloride* melts at 176°, and the red *dichromate* at 146°.

C. H. D.

Derivatives of *p*-Iodoazobenzene and *m*-Chloroiodobenzene with Polyvalent Iodine. Conrad Willgerodt and George McPhail Smith (*Ber.*, 1904, 37, 1311—1317. Compare Abstr., 1903, i, 743, 745, 746; preceding abstract).—*p*-Iodoazobenzene (Noelting and Werner, Abstr., 1891, 211) absorbs chlorine in solutions in chloroform and acetic acid, forming *azobenzene*-p-*iodochloride*, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot ICl_2$, which separates in large, red, monoclinic tablets and decomposes slowly when heated, finally melting at 100°. p-*Iodosoazobenzene*,

$$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot IO,$$

forms a yellowish-red powder, insoluble in most solvents, and melts and decomposes at 105°. The *acetate*, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot I(OAc)_2$, forms rosettes of ruby-red crystals and melts and decomposes at 164°. p-*Iodoxyazobenzene*, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot IO_2$, forms a red, amorphous, insoluble powder and explodes at 189°.

p-*Benzeneazophenyliodinium hydroxide*, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot IPh \cdot OH$, is only obtained in solution. The *chloride* forms rosettes of dark red needles and melts at 205°; the *bromide* forms yellowish-red crystals and melts at 164°; the *iodide* forms long, bright yellow, silky needles and melts at 135°, the *dichromate* and *platinichloride* crystallise from hot water and decompose on heating; the *mercurichloride* crystallises in short, red needles and decomposes at 152—156°. Yellow ammonium sulphide at low temperatures forms a *polysulphide*, closely resembling antimony sulphide, and decomposing above 0° to a heavy oil.

Di-m-*chlorophenyliodinium hydroxide*, $(C_6H_4Cl)_2I \cdot OH$, is obtained in solution from *m*-chloroiodoso- and *m*-chloroiodoxy-benzene (Willgerodt, Abstr., 1893, i, 699). The *chloride* crystallises from water in slender needles and melts at 175—177°; the *bromide* forms colourless needles and melts at 155°; the *iodide* separates from alcohol in colourless needles and melts at 132°; the *dichromate* forms large, orange needles and melts and decomposes at 143°; the *platinichloride* forms golden, glistening leaflets, and the *mercurichloride* forms white needles and melts at 180—182°.

Phenyl-m-*chlorophenyliodinium hydroxide*, $C_6H_4Cl \cdot IPh \cdot OH$, is obtained in solution only. The *chloride* forms long, slightly grey needles and melts at 163°; the *bromide* forms glistening, white needles and melts at 164°; the *iodide* forms small, white needles and melts at 130°; the *dichromate* melts and decomposes at 128°; the *platinichloride* forms orange leaflets and melts and decomposes at 169°, and the *mercurichloride* forms colourless needles and melts at 122—126°.

C. H. D.

Tetrachlorodinitrobenzene. C. Loring Jackson and H. A. Carlton (*Amer. Chem. J.*, 1904, 31, 360—386. Compare Abstr., 1903, i, 79—80).—When 1 : 2 : 3 : 5-tetrachloro-4 : 6-dinitrobenzene is heated with aniline for 3 hours at 100°, it is converted into 2-*chloro*-4 : 6-*dinitro*-1 : 3 : 5-*trianilinobenzene*, $C_6Cl(NO_2)_2(NHPh)_3$, which has a dark red colour, melts at 179°, and is freely soluble in ether, chloroform, acetone, carbon disulphide, hot glacial acetic acid, or hot benzene. This substance has a strong tendency to form additive compounds, in which the added substance appears to be attached similarly to water of crystallisation in salts, and is expelled at 100°. On crystallisation

from benzene, the *compound* $C_6Cl(NO_2)_2(NHPh)_3,C_6H_6$ is obtained as dark crimson plates; the *compound* $2C_6Cl(NO_2)_2(NHPh)_3,C_6H_6$ forms orange-red needles. The toluene *compound*,

$$2C_6Cl(NO_2)_2(NHPh)_3,C_7H_8,$$

crystallises in brilliant, orange-coloured needles. The acetic acid *compound*, $C_6Cl(NO_2)_2(NHPh)_3,C_2H_4O_2$, forms long, orange-coloured needles. The chloroform *compound*, $C_6Cl(NO_2)_2(NHPh)_3,CHCl_3$, crystallises in dark red prisms and gradually loses chloroform at the ordinary temperature. An attempt was made to prepare the chloride of chlorodinitrotrianilinobenzene, but without success.

2-Chloro-1 : 3 : 5-tribromobenzene melts at 90—91°. On nitration, it yields 2-*chloro*-1 : 3 : 5-*tribromo*-4 : 6-*dinitrobenzene*, which crystallises in white prisms, melts at 208°, is freely soluble in ether, benzene, chloroform, acetone, carbon disulphide, or hot glacial acetic acid, and by the action of aniline is converted into chlorodinitrotrianilinobenzene, identical with that obtained from tetrachlorodinitrobenzene.

When a solution of tetrachlorodinitrobenzene in benzene is boiled for 10 minutes with sodium ethoxide, chlorodinitrophloroglucinol diethyl ether is produced together with *tetrachlororesorcinol diethyl ether*, $C_6Cl_4(OEt)_2$, which crystallises from alcohol in white, slender needles, melts at 73°, and is freely soluble in ether, benzene, chloroform, light petroleum, acetone, glacial acetic acid, or carbon disulphide.

By the action of ethyl sodiomalonate on tetrachlorodinitrobenzene, *ethyl trichlorodinitrophenylmalonate*, $C_6Cl_3(NO_2)_2\cdot CH(CO_2Et)_2$, is obtained, which crystallises from alcohol in short, white prisms, melts at 82°, and dissolves readily in ether, benzene, chloroform, acetone, glacial acetic acid, or carbon disulphide. When the crude product of this reaction is distilled with steam, the residue contains a substance which is probably *ethyl trichlorodinitrophenylacetate*,

$$C_6Cl_3(NO_2)_2\cdot CH_2\cdot CO_2Et,$$

which crystallises from alcohol in long, slender, white needles, melts at 87—88°, and is easily soluble in ether, benzene, chloroform, acetone, glacial acetic acid, or carbon disulphide; the corresponding *acid* crystallises in white prisms, melts at 190—191°, and dissolves readily in alcohol, ether, chloroform, or acetone; its silver *salt* is of a pale yellow colour. E. G.

Nitration of Fluorobenzene. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 659—665. Compare this vol., i, 232).—Whilst *p*-fluoronitrobenzene is quantitatively converted into *p*-nitroanisole by the action of sodium methoxide, *m*-fluoronitrobenzene is hardly acted on at all when treated with sodium methoxide under the same conditions. It is thus possible to determine quantitatively the amounts of *p*- and *m*-fluoronitrobenzene in a mixture containing the two. Similarly, 1-fluoro-2 : 4-dinitrobenzene can be separated from *p*-fluoronitrobenzene, and it is accordingly possible to estimate any fluoro-di- or -*m*-nitrobenzene present in the nitration product of fluorobenzene. *o*-Fluoronitrobenzene is readily converted into the dinitro-compound. The product, formed by

nitrating 10 grams of fluorobenzene at 0° with a mixture of 25 c.c of nitric acid of sp. gr. 1·48 and 5 c.c. of nitric acid of sp. gr. 1·51, consists of 6·1 per cent. of *o*-fluoronitrobenzene, 4·1 per cent. of *m*-nitrobenzene fluoride, and 89·8 per cent. of *p*-fluoronitrobenzene; on further nitration of this product, a mixture containing 9 per cent. of fluorodinitrobenzene, 4 per cent. of the meta- and 87 per cent. of the para-compound.

The product obtained by nitrating fluorobenzene at −30° is similar to that obtained at 0°. A. McK.

Additive Compounds of *s*-Trinitrobenzene. Pieter van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 702. Compare Hibbert and Sudborough, Trans., 1903, 83, 1334).—*s*-Trinitrobenzene combines with anthracene to form orange-red needles melting at 161°, with methylanthracene to form red needles melting at 138°, with phenanthracene to form an orange-yellow compound melting at 163°, and with fluorene to form a yellow compound; in those cases, 1 mol. of *s*-trinitrobenzene is combined with 1 mol. of the hydrocarbon.

s-Trinitrobenzene forms with *a*-bromonaphthalene a lemon-yellow compound melting at 139°, and a similar one with dibenzylideneacetone.

s-Trinitrobenzene also interacts with anthranilic acid, methylanthranilate, *p*-aminoacetophenone, ethyl *m*-aminobenzoate, and ethyl *p*-aminobenzoate to form coloured crystalline compounds. A. McK.

Formation and Decomposition of Diphenylmethane Derivatives. Karl Auwers (*Ber.*, 1904, 37, 1470—1479).—A theoretical discussion of the formation of diphenylmethane derivatives from the *ψ*-phenols. E. F. A.

Arylated Ethylenes and their Reduction to Arylparaffins. August Klages and Sebastian Heilmann (*Ber.*, 1904, 37, 1447—1457. Compare Abstr., 1902, i, 668; Hell and Stockmayer, this vol., i, 241). —*as*-Diphenylethylene is oxidised by air with formation of formaldehyde, which, in a glass vessel, polymerises to trioxymethylene (Tiffeneau, Abstr., 1903, i, 81).

aβ-Diphenylpropane, obtained by reduction of *aβ*-diphenylpropylene, boils at 285—286° (corr.) (see Silva, Abstr., 1880, 259; Krämer, Spilker, and Eberhardt, Abstr., 1891, 207).

Diphenylpropylcarbinol, $CH_2Et{\cdot}CPh_2{\cdot}OH$, formed by the action of benzophenone on magnesium propyl iodide, melts at 65° and boils at 162—163° under 11 mm. pressure. The *chloride*, $CH_2Et{\cdot}CPh_2{\cdot}Cl$, is a yellow oil, and when heated with pyridine at 125° yields *aa*-diphenylbutylene, $CPh_2{:}CHEt$, which is a colourless oil, boils at 154° under 20 mm., at 286° (corr.) under 750 mm. pressure, and has a sp. gr. 1·030 at 18°/4°. It decolorises potassium permanganate solution and forms an additive compound with bromine.

aa-Diphenylbutane, obtained by reduction of diphenylpropylcarbinol with zinc dust and a mixture of glacial acetic acid and hydriodic acid, or with hydriodic acid and red phosphorus, boils at 140—142°

under 11 mm., at 265—266° under 751 mm. pressure. *αα*-Diphenylbutylene is only slightly reduced by sodium and alcohol (compare Masson, Abstr., 1903, i, 21).

Phenylbenzylethylcarbinol, $CH_2Ph{\cdot}CEtPh{\cdot}OH$, obtained from ethyl iodide and deoxybenzoin, is a colourless, viscid oil which boils at 179° under 14 mm. pressure. The *chloride*, formed by the action of thionyl chloride on the carbinol, yields *αβ*-diphenylbutylene when heated with pyridine at 172°. *αβ-Diphenylbutylene*, $CHPh{:}CEtPh$, distils in two fractions, at 164—167° and 168°. After some days, the two oils deposit thick, strongly refractive crystals which melt at 57°; the resulting liquid distils at 296—297°, yielding an oil which again slowly deposits crystals. The crystalline and liquid diphenylbutylenes are considered to be probably *cis*- and *trans*-isomerides (compare Sudborough, Abstr., 1892, 1224). Both isomerides yield additive compounds with bromine, and are oxidised by potassium permanganate and dilute sulphuric acid to benzoic acid and phenyl ethyl ketone.

αβ-Diphenylbutane, obtained by reduction of *αβ*-diphenylbutylene, is a colourless, odourless oil which boils at 152° under 11 mm., or at 288—289° under 751 mm. pressure.

Diphenylhexylcarbinol, $(C_6H_{13}){\cdot}CPh_2{\cdot}OH$, formed by the action of phenyl hexyl ketone on magnesium phenyl bromide, is a colourless oil which boils at 200—201° under 11 mm. pressure.

αα-Diphenylheptylene, $CPh_2{:}CH{\cdot}C_5H_{11}$, formed from the carbinol through the chloride, is a colourless oil having a slight odour, has a sp. gr. 0·9673 at 18°/4°, and n_D 1·5648, and is only slightly soluble in alcohol. The action of bromine on diphenylheptylene in carbon disulphide solution leads to the formation of an oily *dibromide*, in glacial acetic acid solution to evolution of hydrogen bromide and formation of a *monobromo*-derivative, $CPh_2{:}CBr{\cdot}C_5H_{11}$, which crystallises in delicate needles and melts at 74°.

αα-Diphenylheptane, obtained by reduction of the heptylene, is a colourless oil which boils at 180° under 10 mm., at 333—334° (corr.) under 751 mm. pressure, and is perhaps identical with Auger's diphenylheptane (Abstr., 1887, 814).

Diphenylbenzylcarbinol (Hell and Wiegandt, this vol., i, 490) is formed by the action of deoxybenzoin or of ethyl phenylacetate on magnesium phenyl bromide. The *chloride* is a colourless oil, which, when heated with pyridine, yields *triphenylethylene*; this melts at 62°, distils at 220—221° under 14 mm., or at 348—349° (corr.) under 751 mm. pressure, and yields a *dibromide* which melts at 92°. Triphenylethane, obtained by reduction of triphenylethylene, is identical with Biltz' triphenylethane formed from triphenylvinyl alcohol (Abstr., 1897, i, 533).

Phenyldibenzylcarbinol, $CPh(CH_2Ph)_2{\cdot}OH$, formed by the action of ethyl benzoate on magnesium benzyl chloride, crystallises in small, colourless needles and melts at 86—87°.

Tribenzylcarbinol, $C(CH_2Ph)_3{\cdot}OH$, formed by the action of ethyl phenylacetate on magnesium benzyl chloride, crystallises in broad, glistening needles, melts at 114—115°, and boils at 383° (corr.) under 753 mm. pressure. It is probably identical with Houben's product, melting at 108—111° (Abstr., 1903, i, 826). G. Y.

Specific Gravity and Thermal Expansion of Solutions of Naphthalene in Various Organic Solvents. CARL FORCH (*Festschr. Ludwig Boltzmann*, 1904, 696—705. Compare Abstr., 1903, ii, 632).—The solvents employed were chloroform, toluene, carbon disulphide, and ether. The value of the expression $(s-Q)/m$, where s and Q are the specific gravities of solution and solvent respectively and m is the molecular concentration of the naphthalene, increases with falling concentration in toluene, carbon disulphide, or ether; in chloroform solutions, the reverse is the case. In every case, the specific gravity observed is less than is to be expected from the specific gravities of the solvent and of solid naphthalene; that is, there is an increase of the molecular volumes. A noteworthy illustration of this is the fact that a 32 per cent. solution of naphthalene in carbon disulphide is lighter than solid naphthalene. J. C. P.

Triphenylmethyl. VIII. MOSES GOMBERG (*Ber.*, 1904, 37, 1626—1644. Compare Abstr., 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244, 472; this vol., i, 32).—Substituted triphenylmethyl compounds have been obtained by the action of metals on substituted triphenylcarbinol chlorides. Most of these have not been isolated in the free form, but as peroxides.

Tri-*p*-tolylchloromethane, obtained by Friedel-Craft's synthesis or by Grignard's reaction, when treated in benzene solution with finely-divided (molecular) silver in the absence of air, yields an orange-yellow solution which contains a strongly unsaturated compound. When the solution is kept, the colour disappears, the unsaturated characteristics are no longer exhibited, and, on evaporation, a syrup corresponding in composition and molecular weight with *hexatolylethane* is obtained. If a current of air is passed through the benzene solution of the tritolylchloromethane in the presence of silver, *tri*-p-*tolylmethyl peroxide*, $O_2[C(C_6H_4Me)_3]_2$, is obtained, the yield varying from 20—40 per cent. It crystallises from hot benzene or hot ether in large, glistening crystals melting at 169—170°. The same product is obtained when tritolylchloromethane in benzene solution is oxidised with an aqueous sodium peroxide solution in the presence of a little acetic acid. Hydrolysis with a mixture of sulphuric and acetic acid yields the carbinol.

[With A. J. LYNN.]—*Phenyldi*-p-*tolylchloromethane* melts at 106—107° and the corresponding carbinol at 79—80°. The *peroxide*,

$$O_2[CPh(C_6H_4Me)_2]_2,$$

is soluble in ether, but insoluble in light petroleum, and melts at 147—148°.

Diphenyl-*p*-tolylchloromethane, obtained from benzophenone chloride, toluene, and ferric chloride in the presence of carbon disulphide, may be converted into a *peroxide*, $O_2(CPh_2{\cdot}C_6H_4Me)_2$, melting at 170—171°.

p-Chlorotriphenylchloromethane, $C_6H_4Cl{\cdot}CPh_2Cl$, obtained from benzophenone chloride, chlorobenzene, and aluminium chloride or from *p*-chlorobenzophenone chloride (Overton, Abstr., 1893, i, 208) and benzene with aluminium chloride, melts at 87° and gives a *peroxide* melting at 165° and insoluble in ether. p-*Bromotriphenylchloromethane*

melts at 111° and the *peroxide* obtained from it at 167°; the corresponding p-*iodo*-compound melts at 119° and the *peroxide* at 169°.

[With L. H. Cone.]—*Tri*-p-*chlorotriphenylchloromethane*,

$$CCl(C_6H_4Cl)_3,$$

obtained from carbon tetrachloride, chlorobenzene, and aluminium chloride under certain conditions, melts at 146—148° and yields a *peroxide* (?) melting at 140—142°.

Diphenyl-α-naphthylchloromethane, obtained from benzophenone chloride, naphthalene, and aluminium chloride in presence of carbon disulphide, melts at 169°. It dissolves in concentrated sulphuric acid yielding a bluish-green solution and evolving hydrogen chloride. The *peroxide* is obtained as a crystalline precipitate insoluble in most organic solvents.

Tri-p-*nitrophenylcarbinol chloride* may be obtained by the action of phosphorus pentachloride on the corresponding carbinol at 170—180°. The carbinol melts at 189° (E. and O. Fischer, *Annalen*, 1878, **194**, 255, gave 171—172°) and when pure dissolves in alkalis to a colourless solution. The peroxide obtained by the action of silver on solutions of the carbinol chloride in ethyl acetate and subsequent oxidation by atmospheric oxygen appears to be identical with the compound previously described (Abstr., 1901, i, 78), although it melts at 218°.

Comparative experiments in the rates of polymerisation of certain of these triphenyl methyl derivatives have been conducted by keeping the benzene solutions in sealed tubes for some time and noticing the loss of colour and of the unsaturated properties.

Although triphenylmethyl in solution has been shown to be bimolecular, this is attributed to association, and the simple formula CPh_3 is retained. J. J. S.

α-Phenylstilbene and the Methylene Ether of 3 : 4-Dihydroxystilbene. Carl Hell and Fr. Wiegandt (*Ber.*, 1904, **37**, 1429—1432. Compare this vol., i, 242).—Benzophenone, either fused or in ethereal solution, is added to an ethereal solution of magnesium benzyl chloride, and, after treatment with dilute hydrochloric acid, the ether is distilled off. The fraction of the residue distilling at 200—240° under 12—15 mm. pressure contains diphenylbenzylcarbinol. If the residue is heated to 300° before distillation, the fraction distilling at 200—240° is α-phenylstilbene.

Diphenylbenzylcarbinol, $CH_2Ph{\cdot}CPh_2{\cdot}OH$, crystallises in long, glistening needles and melts at 88—89°.

α-*Phenylstilbene*, $CHPh{:}CPh_2$, crystallises in small leaflets, melts at 67—68°, and forms an additive compound with bromine, which easily loses hydrogen bromide.

The action of piperonal on magnesium benzyl chloride leads to the formation of the *methylene ether* of 3 : 4 dihydroxystilbene,

$$CHPh{:}CH(C_6H_3{:}O_2{:}CH_2),$$

which distils at 225—250° under 12 mm. pressure, crystallises in glistening needles, and melts at 95—96°.

The *dibromide*, obtained by the action of bromine on the methylene ether in chloroform solution, forms small, white crystals and melts at 188°. G. Y.

A Quinonoid Hydrocarbon. JOHANNES THIELE and HANS BALHORN (*Ber.*, 1904, **37**, 1463—1470).—*ω-Hexabromo*-p-*xylene*, $CBr_3 \cdot C_6H_4 \cdot CBr_3$, crystallises in needles melting at 187—190°. *p*-Dibenzylbenzene is best prepared by condensing formaldehyde with benzene, using ethyl acetate as the solvent; by the action of bromine in chloroform, *diphenyl*-p-*xylylene bromide* is formed, which, after repeated crystallisation, melts at 112·5°. Silver or mercury act on this, forming yellow solutions which undoubtedly contain *diphenyl*-p-*xylylene*, $CHPh \colon C_6H_4 \colon CHPh$, but this could not be isolated.

Tetraphenyl p-*xylyleneglycol dimethyl ether*,

$$OMe \cdot CPh_2 \cdot C_6H_4 \cdot CPh_2 \cdot OMe,$$

prepared by the interaction of magnesium phenyl bromide and methyl terephthalate, melts at 181—182·5°; by bromine in acetic acid solution, it is converted into *tetraphenyl*-p-*xylylene bromide*, $CPh_2Br \cdot C_6H_4 \cdot CPh_2Br$, which crystallises in colourless plates, melts and decomposes at 270—272°, and dissolves in concentrated sulphuric acid with a deep orange coloration.

The hydrocarbon, *tetraphenyl*-p-*xylylene* (1 : 4-*bisdiphenylmethylene*-$\Delta^{2,5}$-cyclo*hexadiene*), $CPh_2 \colon C<\begin{matrix} CH \colon CH \\ CH \colon CH \end{matrix}>C \colon CPh_2$, is prepared by boiling the bromide with silver in benzene solution in the dark. It forms glistening, orange-yellow needles, melts and decomposes at 239—242°, is sparingly soluble in all solvents, forms yellow or orange solutions which have a golden-yellow fluorescence and rapidly become colourless when exposed to light. It takes up bromine instantaneously, is rapidly reduced by aluminium amalgam, and liberates iodine from hydrogen iodide. E. F. A.

Oxygen Ethers of Carbamides. W. M. BRUCE (*J. Amer. Chem. Soc.*, 1904, **26**, 419—436).—m-*Nitrobenzoylthiocarbimide*,

$$NO_2 \cdot C_6H_4 \cdot CO \cdot NCS,$$

obtained by the action of *m*-nitrobenzoyl chloride on lead thiocyanate, melts at 94°. When heated with methyl alcohol, it is converted into *methyl* m-*nitrobenzoyliminothiocarbonate*, $NO_2 \cdot C_6H_4 \cdot CO \cdot N \colon C(SH) \cdot OMe$, which forms yellow crystals and melts at 120°; its *potassium* salt decomposes at about 260°. *Methyl ethyl* m-*nitrobenzoyliminothiocarbonate*, $NO_2 \cdot C_6H_4 \cdot CO \cdot N \colon C(SEt) \cdot OMe$, crystallises in needles and melts at 78°. If this compound is treated with aniline, mercaptan is evolved and s-m-*nitrobenzoylphenyl*iso*carbamide methyl ether*,

$$NO_2 \cdot C_6H_4 \cdot CO \cdot N \colon C(OMe) \cdot NHPh,$$

is produced, which crystallises in colourless needles and melts at 124°. The last-mentioned substance is more readily prepared by the action of *m*-nitrobenzoyl chloride on phenyl*iso*carbamide methyl ether. When heated with dry hydrogen chloride, it suffers decomposition with formation of methyl chloride and s-m-*nitrobenzoylphenylcarbamide*, $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CO \cdot NHPh$, which crystallises in colourless needles, melts at 224°, and is soluble in hot water. When the methyl ether of *m*-nitrobenzoylphenyl*iso*carbamide is boiled with solution of potassium hydroxide, the free *iso*carbamide is not obtained, but decomposition occurs with production of *m*-nitrobenzoic acid and aniline.

s-Benzoylphenyl*iso*carbamide methyl ether, $NBz \colon C(OMe) \cdot NHPh$,

crystallises in slender needles, melts at 50°, and is completely decomposed by boiling potassium hydroxide solution. Its *silver* derivative,

$$C_6H_5 \cdot C(OAg){:}N \cdot C(OMe){:}NPh,$$

was prepared and analysed. The *hydrochloride* of benzoyl*iso*carbamide methyl ether, $NHBz \cdot C(OMe){:}NH,HCl$, is unstable, and gradually undergoes decomposition with loss of methyl chloride; the *sodium* salt, $C_6H_5 \cdot C(ONa){:}N \cdot C(OMe){:}NH$, was also prepared.

By the action of acetyl chloride on phenyl*iso*carbamide methyl ether, a mixture of isomeric acetyl derivatives is produced. s-*Acetylphenyl*-iso*carbamide methyl ether*, $NHAc \cdot C(OMe){:}NPh$, is obtained as an oil which is decomposed by dry hydrogen chloride with formation of methyl chloride and *s*-acetylphenylcarbamide; its *platinichloride* was prepared and analysed. as-*Acetylphenyl*iso*carbamide methyl ether*,

$$NPhAc \cdot C(OMe){:}NH,$$

crystallises in long, rhombic prisms, melts at 102°, and is readily soluble in chloroform, benzene, alcohol, acetone, or ether; it slowly undergoes rearrangement into the *s*-isomeride, and is readily hydrolysed with formation of phenyl*iso*carbamide methyl ether; its *hydrochloride* was prepared and analysed. When the *as*-compound is treated with dry hydrogen chloride, methyl chloride is evolved and as-*acetylphenyl-carbamide*, $NPhAc \cdot CO \cdot NH_2$, is produced, which crystallises from hot water in slender needles and melts at 167°.

When the *silver* salt of phenyl*iso*carbamide methyl ether,

$$AgN{:}C(OMe) \cdot NHPh,$$

is treated with acetyl bromide, *s*-acetylphenylcarbamide methyl ether is produced. The *silver* salts of phenyl*iso*carbamide ethyl ether, *s*-acetyl-phenyl*iso*carbamide methyl ether, and acetyl*iso*carbamide methyl ether were also prepared.

*Acetyl*iso*carbamide methyl ether*, $NAc{:}C(OMe) \cdot NH_2$, crystallises from light petroleum and melts at 58·5°. m-*Nitrobenzoyl*iso*carbamide methyl ether*, $NO_2 \cdot C_6H_4 \cdot CO \cdot N{:}C(OMe) \cdot NH_2$, crystallises in slender needles and melts at 115°. E. G.

p-Acetylaminophenylcarbamidohydroxynaphthylsulphonic Acid. Gesellschaft für Chemische Industrie in Basel (D.R.-P. 148505).—When phosgene gas is passed into a solution of 6-amino-*a*-naphthol-3-sulphonic acid, *p*-aminoacetanilide, and sodium acetate, 6-p-*acetylaminophenylcarbamido*-1-*hydroxynaphthyl*-3-*sulphonic acid*,

$$SO_3H \cdot C_{10}H_5(OH) \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot NHAc,$$

is formed as a greyish-white powder, dissolving sparingly in cold, readily in hot water, and precipitated from its alkaline solutions by dilute acids. It combines with solutions of diazonium salts to form orange azo-compounds, which are hydrolysed by dilute sodium hydroxide. C. H. D.

Viscosity of Mixtures of Water and Phenol. Oscarre Scarpa (*Nuovo Cimento*, 1903, [v], 6, 277—288. Compare Abstr., 1903, ii, 640).—The author has made measurements of the viscosity of mixtures of water and phenol of various compositions at five different temperatures ranging from 67·5° to 85°, and has constructed the corresponding viscosity-composition curves. All these curves show two changes of

curvature at the points corresponding with about 58 and 15 per cent. respectively of phenol in the solution. T. H. P.

Action of Sulphur and of Selenium on the Organo-magnesium Compounds of Mono- and Di-halogenated Aromatic Hydrocarbons. F. Taboury (*Compt. rend.*, 1904, 138, 982—983).—In addition to the thiophenols and disulphides already described (compare Abstr., 1903, i, 748), prepared by the interaction of sulphur and an aryl magnesium haloid, the following have also been obtained: from bromophenyl magnesium bromide, thiobromophenol and bromophenyl disulphide; from chlorophenyl magnesium bromide, thiochlorophenol and chlorophenyl disulphide; from bromonaphthyl magnesium bromide, thiobromonaphthol and bromonaphthyl disulphide; from chloronaphthyl magnesium bromide, thiochloronaphthol and chloronaphthyl disulphide. By the interaction of the above organo-magnesium compounds and benzoyl chloride, the following thiobenzoates have been obtained: *bromonaphthyl thiobenzoate*, $C_{10}H_6Br\cdot S\cdot COPh$, melting at 120—121°; *chloronaphthyl thiobenzoate*, $C_{10}H_6Cl\cdot S\cdot COPh$, melting at 111—112°; *bromophenyl thiobenzoate*, $C_6H_4Br\cdot S\cdot COPh$, melting at 83—84°, and *chlorophenyl thiobenzoate*, $C_6H_4Cl\cdot S\cdot COPh$, melting at 75—76°. M. A. W.

Chlorination of Phenyl Carbonate in the presence of Iodine. Étienne Barral (*Compt. rend.*, 1904, 138, 909—911).—All the chloro-derivatives of phenyl carbonate can be obtained either by direct chlorination of phenyl carbonate in the presence of a chlorine carrier, such as iodine, aluminium chloride, antimony pentachloride, or ferric chloride under suitable conditions of temperature (compare Abstr., 1898, i, 575) or synthetically from phosgene gas and the chlorinated phenols (compare Abstr., 1899, i, 747; 1901, i, 28). By the first method, and using iodine as a chlorine carrier, the following derivatives were obtained: (1) at the ordinary temperature or at 90°, phenyl *p*-chlorophenyl carbonate, $OPh\cdot CO\cdot O\cdot C_6H_4Cl$, melting at 95—96° and crystallising in white, silky, pearly needles (compare Morel, *Thèse de Paris*, 1900); *p*-chlorophenyl carbonate, $CO(O\cdot C_6H_4Cl)_2$, melting at 144—145° and not at 142° as stated in the earlier paper; (2) at 140°, p-*chlorophenyl* 2 : 4-(?)-*dichlorophenyl carbonate*,

$$C_6H_4Cl\cdot O\cdot CO\cdot O\cdot C_6H_3Cl_2,$$

crystallising in white, pearly needles melting at 115°, a small quantity of an isomeride melting at about 100°, and two isomeric 2 : 4-dichlorophenyl carbonates, $CO(O\cdot C_6H_3Cl_2)_2$, one (α-) melting at 122—123°, and the other (β-) melting at 88—89°; (3) at 150—155°, and by continuing the chlorination for a month, a mixed *di-* and *tri-chlorophenyl carbonate*, $C_6H_3Cl_2\cdot O\cdot CO\cdot O\cdot C_6H_2Cl_3$, crystallising in white needles and melting at 94°, and 2 : 4 : 6-*trichlorophenyl carbonate*,

$$CO(O\cdot C_6H_2Cl_3)_2,$$

forming cauliflower-like clusters of hard needles melting at 153—154°, and less soluble than the preceding. M. A. W.

Chlorination of Phenyl Carbonate in the presence of Antimony Chloride. Étienne Barral (*Compt. rend.*, 1904, 138, 980—982).—In the presence of iodine, the chlorination of phenyl car-

bonate cannot be carried farther than the trichloro-derivative (compare preceding abstract), and attempts to prepare the higher derivatives by using aluminium chloride instead of iodine as a chlorine carrier were unsuccessful owing to the decomposition which occurred at the high temperature. In the presence of antimony chloride, however, at temperatures varying between 90° and 200°, in addition to the derivatives already obtained by the use of iodine, the following higher chlorinated derivatives of phenyl carbonate have been prepared: (1) a mixed *di-* and *tri-chlorophenyl carbonate*, $C_6H_3Cl_2{\cdot}O{\cdot}CO{\cdot}O{\cdot}C_6H_2Cl_3$, crystallising in white needles melting at 130°; (2) 2 : 4 : 6-*trichlorophenyl* 2 : 3 : 4 : 6-*tetrachlorophenyl carbonate*, $C_6H_2Cl_3{\cdot}O{\cdot}CO{\cdot}O{\cdot}C_6HCl_4$, crystallising in white, pearly needles melting at 175—176°; (3) 2 : 3 : 4 : 6-*tetrachlorophenyl carbonate*, $CO(O{\cdot}C_6HCl_4)_2$, crystallising in cauliflower-like clusters of pearly needles melting at 155—156°, also obtained synthetically from phosgene and potassium tetrachlorophenoxide; (4) 2 : 3 : 4 : 6-*tetrachlorophenyl pentachlorophenyl carbonate* $C_6HCl_4{\cdot}O{\cdot}CO{\cdot}O{\cdot}C_6Cl_5$, forming white needles melting at 168—169°, and (5) *pentachlorophenyl carbonate* $CO(O{\cdot}C_6Cl_5)_2$, crystallising in white, translucent prisms melting at 258°, almost insoluble in neutral solvents, slightly soluble in cold benzene, more so on boiling; this compound has also been synthesised from phosgene and potassium pentachlorophenate. M. A. W.

Derivatives of β-Amino-orcinol. FERDINAND HENRICH, W. MEYER, and KARL DORSCHKY (*Ber.*, 1904, **37**, 1425—1428. Compare Abstr., 1903, i, 413).—*β-Amino-orcinol picrate*, $C_{13}H_{12}O_9N_4$, crystallises from hot aqueous solutions in greenish-yellow needles containing $1H_2O$, which it loses at 105°. It darkens at 140° and begins to decompose at 190°. The *acid sulphate*, $C_8H_9O_2N,H_2SO_4$, is sparingly soluble in water. The *ferrocyanide*, $4C_7H_9O_2N,H_4FeC_6N_6$, forms a brown precipitate. The *normal oxalate* crystallises in needles. Bromine reacts with an acetic acid solution of the hydrochloride yielding a *dibromo*-derivative, the *hydrochloride* of which is sparingly soluble in cold water and may be crystallised from glacial acetic acid. The dibromo-hydrochloride, on treatment with acetic anhydride and subsequent hydrolysis with alcoholic potash, yields 4 : 6-*dibromo-5-hydroxy-*1 : 3-*dimethylbenzoxazole*, $\begin{array}{l}OH{\cdot}C{=\!=\!=}CBr{\cdot}C{\cdot}O\\ \quad | \qquad\qquad\ \ \|\\ \ \ CBr{:}CMe{\cdot}C{\cdot}N\end{array}\!\!>CMe$, melting at 221—222° and only sparingly soluble in ether or light petroleum.

Hypochlorous acid transforms β-amino-orcinol hydrochloride into a *compound* $C_7H_7O_4Cl_3$, which crystallises in needles and melts at 97°. It dissolves in alkalis. A second *compound* $C_7H_6O_4Cl_2$, melting at 117°, is also formed. J. J. S.

Action of Magnesium and Organo-magnesium Compounds on Bromophenetole. VICTOR GRIGNARD (*Compt. rend.*, 1904, **138**, 1048—1050. Compare Abstr., 1902, i, 142, 198, 420; 1903, i, 31, 141, 455, 549, 552; this vol., i, 213; Hamonet, this vol., i, 401).—Bromophenetole reacts with magnesium on warming in the presence of dry ether to form ethylene and a crystalline derivative which, on hydrolysis, furnishes phenol; probably the normal magnesium compound is first formed, and breaks down

according to the equation $OPh\cdot CH_2\cdot CH_2\cdot MgBr = OPh\cdot MgBr + CH_2{:}CH_2$. A small quantity of $\alpha\delta$-diphenoxybutane, $C_4H_8(OPh)_2$, crystallising in plates melting at 98°, is also formed. Bromophenetole reacts abnormally with magnesium amyl bromide to form phenol and amyl alcohol, and normally with magnesium phenyl bromide, giving a little phenol and 83 per cent. of the phenyl ether of benzylcarbinol, $OPh\cdot CH_2\cdot CH_2Ph$ (compare Abstr., 1903, i, 819; and Tiffeneau and Delange, this vol., i, 48), which is a liquid boiling at 166° under 14 mm. pressure, and converted by heating with hydrobromic acid in an autoclave at 120° into β-phenylethyl bromide, $CH_2Ph\cdot CH_2Br$, boiling at 92° under 11 mm., and at 217—218° under 734 mm. pressure, and reacting with magnesium to form the normal magnesium derivative together with a little styrene and diphenylbutane; the magnesium derivative reacts with carbon dioxide to form phenylpropionic acid melting at 48° (50 per cent.), and is oxidised by a current of oxygen giving benzylcarbinol (60 per cent.) boiling at 102° under 13 mm. and 220° under 750 mm. pressure (compare Tiffeneau and Delange, this vol., i, 48). Bromophenetole reacts with magnesium benzyl chloride at 100° to form phenol, benzyl alcohol, and a small quantity of the phenyl ether of phenylpropyl alcohol,

$$CH_2Ph\cdot CH_2\cdot CH_2\cdot OPh,$$

which boils at 171—172° under 11 mm. pressure, yields β-phenylpropyl bromide, boiling at 110° under 12 mm. pressure, the constitution of which has been established by the formation of phenylbutyric acid, $CH_2Ph\cdot CH_2\cdot CH_2\cdot CO_2H$, melting at 47—48°, by the action of carbon dioxide on the magnesium derivative. M. A. W.

Condensation Products of Aldehydes of the Aliphatic Series with Phenol. A. I. LUNJAK (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 301—311).—The *di*-p-*methoxydiphenylethane*, $C_2H_4(C_6H_4\cdot OMe)_2$, prepared by the action of potassium hydroxide and methyl iodide on a methyl-alcoholic solution of di-*p*-hydroxydiphenylethane, crystallises from ether in plates melting at 59·4° and boiling at 352—354° under 767 mm. pressure. On oxidation with chromic anhydride in acetic acid solution, it yields di-*p*-methoxybenzophenone, anisic acid, and *p*-acetylanisole. From these results, the author concludes that the structure of dihydroxydiphenylethane is $OH\cdot C_6H_4\cdot CHMe\cdot C_6H_4\cdot OH$, the hydroxyl groups being in the para-positions to the central carbon atom.

Di-p-*hydroxydiphenylheptane*, $C_7H_{14}(C_6H_4\cdot OH)_2$, prepared by the condensation of œnanthaldehyde and phenol, separates from light petroleum in pale yellow, microscopic, rhombic plates melting at 103°. Its *dibenzoyl* derivative, $C_7H_{14}(C_6H_4\cdot OBz)_2$, is deposited from dilute alcohol in star-shaped aggregates of microscopic, acicular crystals melting at 106°. The *dimethyl ether*, $C_7H_{14}(C_6H_4\cdot OMe)_2$, is a liquid of sp. gr. 1·02496 at 15°/4°, and, on oxidation with chromic anhydride in acetic acid, yields *p*-dimethoxybenzophenone and anisic acid. T. H. P.

Action of Dilute Nitric Acid on Haloid Compounds. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 220—223).—The

author's investigations on the action of dilute nitric acid on halogen compounds of various types lead to the following conclusions: (1) the haloid compounds of saturated character enter into reaction with dilute nitric acid more readily than the corresponding hydrocarbons. (2) The primary and secondary haloid compounds yield either nitro-products or oxidation products, in both cases containing halogens. The readiness of formation and character of the nitro-compounds formed under these conditions varies with the structure of the hydrocarbon radicle. (3) Tertiary, non-aromatic, haloid compounds, under the action of dilute nitric acid, very readily give up hydrogen haloid, forming unsaturated hydrocarbons which may then undergo nitration.

T. H. P.

Action of Nitric Acid on Alcohols. II. MICHAEL I. KONOWALOFF and N. MANEWSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 224—227. Compare Abstr., 1901, i, 249).—The action of dilute nitric acid on benzyldimethylcarbinol leads first to the removal of water from, and oxidation of, the alcohol, yielding benzaldehyde and benzoic acid; this result would be expected, supposing that the nitric acid acts most rapidly on the carbon group combined immediately with the phenyl. The oxime and secondary nitro-compound also probably result from this action of nitric acid. This removal of water by dilute nitric acid is evidently a general reaction for tertiary alcohols, with the exception of phenols. A similar action is evidenced between dilute nitric acid and tertiary haloid compounds (see preceding abstract). Simultaneously with the removal of water from the alcohol proceeds the nitration of the unsaturated hydrocarbon thus formed. The formation of the primary nitro-compound obtained in this way confirms the views of Konowaloff on the nitration of unsaturated hydrocarbons (*J. Russ. Phys. Chem. Soc.*, 1894, 26, 382). T. H. P.

Synthesis of Alcohols by means of Organo-magnesium Compounds. II. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 228—232. Compare Abstr., 1902, i, 336).—Other alcohols prepared by the author by Grignard's method (Abstr., 1900, i, 382) are the following:

Benzyldimethylcarbinol (compare Grignard, Abstr., 1901, i, 679), which boils at 214—216° at the ordinary pressure, and has the sp. gr. 0·9823 at 15°/0° and n_D 1·5201 at 15°.

Benzyldiethylcarbinol, $CH_2Ph\cdot CEt_2\cdot OH$, obtained from magnesium benzyl chloride and diethyl ketone, boils at 245°.

Benzylmethylethylcarbinol, $CH_2Ph\cdot CMeEt\cdot OH$, prepared from magnesium benzyl chloride and methyl ethyl ketone, boils, decomposing slightly, at 235—238°, has the sp. gr. 0·9927 at 0°/0° and 0·9754 at 20°/0° and n_D 1·51817 at 20°.

*Methylethyl*isoamyl*carbinol*, $C_5H_{11}\cdot CMeEt\cdot OH$, obtained from magnesium *iso*amyl chloride and methyl ethyl ketone, boils at 174—176° and has the sp. gr. 0·8286 at 16°/0° and n_D 1·43256 at 16°.

The formation of certain other products in the preparation of alcohols by this method is regarded by the author as due to the action

exerted on the organo-magnesium compounds by the oxygen of the air (Abstr., 1903, i, 249). T. H. P.

Styrenes. V. AUGUST KLAGES (*Ber.*, 1904, 37, 1721—1726. Compare this vol., i, 302).—The aryl group affects the reduction of Δ^{α}-styrenes in the same way as the carboxylic group does the reduction of $\alpha\beta$-unsaturated acids, thus the Δ^{α}-styrenes, corresponding in constitution to $\alpha\beta$-unsaturated acids, which are reduced with difficulty, are not reduced by sodium and alcohol; the effect of the aryl group is modified by the presence of substituting groups. The formation of Δ^{α}-styrenes from β-halogenated benzene hydrocarbons is to be compared to the formation of $\alpha\beta$-unsaturated acids from β-halogen substituted acids.

[With HUGO HAEN.]—Benzyldimethylcarbinol, $CH_2Ph\cdot CMe_2\cdot OH$, prepared by acting with magnesium and methyl iodide on ethyl phenylacetate, forms long, glistening needles, melts at 24° to a viscid, colourless oil, boils at 127—128° under 14 mm. pressure, and has a sp. gr. 0·9774 at 19°/4°; the *phenylurethane* forms long needles and melts at 96°; the *chloride* is an oil which, when heated with pyridine at 125°, forms β-methyl-Δ^{α}-propenylbenzene, $C_6H_5\cdot CH:CMe_2$, which boils at 76—77° under 14 mm., at 181—182° under 761 mm. pressure, has a sp. gr. 0·9022 at 14·5°/4°, and n_D 1·5280, and is not reduced by sodium and alcohol.

Benzyldiethylcarbinol, $CH_2Ph\cdot CEt_2\cdot OH$, is a viscid, odourless oil, that boils at 135° under 16 mm., at 243—245° under 755 mm. pressure, and has a sp. gr. 0·9782 at 19°/4°; the *phenylurethane* melts at 98°; the *chloride* is an oil with a strong odour; when heated, it loses hydrogen chloride. *β-Ethyl-Δ^α-butenylbenzene*, $CHPh:CEt_2$, is a mobile oil, which boils at 97—98° under 13 mm. pressure, at 204—206° with slight decomposition, has a sp. gr. 0·9038 at 18·5°/4° and n_D 1·5182 at 18·5°; it is not reduced by sodium and alcohol. The *dibromide* is an oil, the nitrosyl chloride melts at 99°.

*Phenylethyl*iso*propylcarbinol*, $OH\cdot CEtPr^{\beta}Ph$, obtained from ethyl iodide and butyrylbenzene, boils at 114—116° under 18 mm. pressure, at 224—226° with decomposition, has a sp. gr. 0·9689 at 12·5°/4° and n_D 1·5155; the *chloride* is a mobile oil. *β-Methyl-α-ethyl-Δ^α-propenylbenzene*, $CEtPh:CMe_2$, boils at 83—84° under 15 mm., at 206—207° under 765 mm. pressure, has a sp. gr. 0·8913 at 14·5°/4° and n_D 1·5134, and forms a *dibromide*. The hydrocarbon is very slightly reduced by sodium and alcohol; the product boils at 81—82° under 12 mm. pressure and has a sp. gr. 0·8851 at 15°.

*Phenylpropyl*iso*propylcarbinol*, obtained from magnesium propyl iodide and *iso*butyrylbenzene, boils at 116—117° under 13 mm., at 230—232° under 759 mm. pressure, and has a sp. gr. 0·9681 at 19°/4°. The *chloride* is a mobile oil.

β-Methyl-α-propyl-Δ^α-propenylbenzene, $CPhPr^{\alpha}:CMe_2$, boils at 94—96° under 12 mm., at 210—212° under 755 mm. pressure, has a sp. gr. 0·8897 at 16°/4°, n_D 1·5070 at 16°, and is not reduced by sodium and alcohol. The *dibromide* is an oil. G. Y.

The Parent Carbinol of Rosaniline and its Isomerides. AUGUSTIN BISTRZYCKI and JOSEPH GYR (*Ber.*, 1904, 37, 1245—1253. Compare this vol., i, 315, and Acree, *ibid.*, i, 315, 409).—*Diphenyl-*

o-*tolylcarbinol*, $C_6H_4Me\cdot CPh_2\cdot OH$, prepared by the action of magnesium phenyl bromide on methyl *o*-toluate, separates from alcohol in snow-white crystals and melts at 98°; on reduction with zinc and glacial acetic acid, it is converted into *diphenyl*-o-*tolylmethane*, which crystallises from methyl alcohol in well-formed, six-sided prisms and melts at 82—83°. Hemilian's diphenyl *o*-tolylmethane (m. p. 62°) (Abstr., 1884, 322) is really identical with O. and E. Fischers' diphenyl *m*-tolylmethane melting at 59—59·5°. *Diphenyl* o-*tolylchloromethane*, $C_6H_4Me\cdot CPh_2Cl$, prepared by the action of hydrogen chloride on the carbinol in ethereal solution, crystallises in prisms and melts at 136—137°.

Diphenyl-m-*tolylcarbinol*, prepared from methyl *m* toluate, crystallises from benzene in six-sided, colourless leaflets, melts at 67—68°, and is not identical with the Fischers' diphenyl *m*-tolylcarbinol, which melts at 150° (Abstr., 1879, 386), although, on reduction with zinc and acetic acid, it gives the same diphenyl-*m*-tolylmethane melting at 60·5—61·5° as was obtained by them. On oxidising the hydrocarbon with chromic acid in glacial acetic acid solution, the diphenyl-*m*-tolylcarbinol (m. p. 67—68°) was regenerated. The nature of the Fischers' carbinol is being investigated. W. A. D.

Compounds of Amino-carboxylic Esters with Aromatic Sulphonic Acids. Eduard Ritsert (D.R.-P. 149345 and 150070. Compare this vol., i, 413).—In place of phenolsulphonic acids, the sulphonic acids of phenyl ethers may be combined with amino-carboxylic esters to form soluble salts. Anisolesulphonic acid and ethyl *p*-aminobenzoate combine to form a *salt* $OMe\cdot C_6H_4\cdot SO_3H,NH_2\cdot C_6H_4\cdot CO_2Et$, which crystallises in glistening needles, melts at 188°, and dissolves readily in hot water or alcohol. The *salt* from guaiacolsulphonic acid and ethyl *p*-aminobenzoate crystallises in needles and melts at 175°.

p Amino-carboxylic esters also form soluble salts with the benzenesulphonic acids. *Ethyl* p-*aminobenzoate toluene*-p-*sulphonate* forms prismatic crystals and melts at 185—187°. *Ethyl* p-*aminobenzoate benzene*-m-*disulphonate*, $2NH_2\cdot C_6H_4\cdot CO_2Et,C_6H_4(SO_3H)_2$, forms coarse crystals and decomposes at 235°. *Methyl* m-*amino*-p-*hydroxybenzoate benzene*-m-*disulphonate* forms slender needles and melts and decomposes at 142°. C. H. D.

Conversion of Anthranilodiacetic Acid into Phenylglycine-*o* carboxylic or Anthranilic Acids. Badische Anilin- & Soda-Fabrik (D.R.-P. 149346).—Small quantities of anthranilodiacetic acid, $CO_2H\cdot C_6H_4\cdot N(CH_2\cdot CO_2H)_2$, are always obtained in the preparation of phenylglycine-*o* carboxylic acid from anthranilic acid and chloroacetic acid. It is not readily convertible directly into indoxyl or indoxylic acid, but may be converted by acid, neutral, or alkaline oxidising agents into phenylglycine-*o*-carboxylic acid. It is not always possible to stop the reaction at this stage, and a portion is then further oxidised to anthranilic acid, which may be reconverted into phenylglycine-*o*-carboxylic acid by the action of chloroacetic acid.

C. H. D.

Benzoylpentaglycylaminoacetic Acid. THEODOR CURTIUS and A. BENRATH (*Ber.*, 1904, 37, 1279—1284).—The so-called "γ-acid" obtained by Curtius (Abstr, 1883, 337) as the final product of the action of benzoyl chloride on silver glycine, and also by fusing ethyl hippurate with glycine, is best prepared by the latter method, and proves to be *benzoylpentaglycylaminoacetic acid*,

$$COPh\cdot[NH\cdot CH_2\cdot CO]_5\cdot NH\cdot CH_2\cdot CO_2H.$$

It crystallises from hot water and melts at 280—285°. Concentrated hydrochloric acid hydrolyses it at 100° to benzoic acid and glycine hydrochloride. The *silver* salt forms a bulky precipitate. The *ethyl* ester forms a loose powder and melts and decomposes at 263°. H. Levy has obtained the same ester synthetically from benzoyltriglycylaminoacetic azoimide (Curtius, Abstr., 1902, i, 844) and ethyl glycylglycine (E. Fischer, Abstr., 1901, i, 675).

The mother-liquor from the preparation of the acid, contains benzoyltriglycylaminoacetic acid, ethyl hippurate, and hippurylaminoacetic acid. C. H. D.

Preparation of Phenyl Ether-*o*-carboxylic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 150323).—Phenyl ether-*o*-carboxylic acid (Graebe, Abstr., 1888, 477) is readily prepared by heating phenol with salts of *o*-chlorobenzoic acid in the presence of copper or of copper salts. C. H. D.

Acids obtained on Nitration with Dilute Nitric Acid. I. 3-Methyl-5-*tert.*-Butylbenzoic Acid (1 : 3 : 5). MICHAEL I. KONOWALOFF and ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 232—237).—The oxidation of *tert.*-butylxylene by means of dilute nitric acid yields 3-methyl-5-*tert.*-butylbenzoic acid (compare Baur-Thurgau, Abstr., 1898, i, 523). The *copper* ($+2H_2O$) and *barium* salts were prepared and also the *ethyl* ester, which boils at 268—270° under 743 mm. pressure, has the sp. gr. 0·9896 at 23°/0° and n_D 1·50139 at 23°. T. H. P.

Two Isomeric β-Methylcinnamic Acids. MARC TIFFENEAU (*Compt. rend.*, 1904, 138, 985—987. Compare Schroeter, this vol., i, 415).—Owing to the readiness with which the two isomeric β-methylcinnamic acids (compare Abstr., 1903, i, 241) are hydrogenated to form the corresponding saturated acid, it is probable that the isomerism is stereomeric. The two acids are readily separated owing to the difference of their solubilities in light petroleum or carbon disulphide, and they melt at 129° and 97—98° respectively. The acid melting at 129° distils without decomposition at 170—172° under 14 mm. pressure, yields methylstyrene when heated with barium hydroxide, and is readily hydrogenated by hydrogen iodide in the presence of phosphorus.

The acid melting at 97—98°, also prepared by saponifying the ethyl methylcinnamate obtained by the condensation of acetophenone and ethyl iodoacetate in the presence of magnesium, distils without decomposition at 171—174° under 15 mm. pressure, yields α-methyl-

styrene when heated with barium hydroxide, and is hydrogenated by hydrogen iodide in the presence of phosphorus to form a saturated acid boiling at 274—276°; the *methyl* ester boils at 259—260°, forms leafy crystals from alcohol, melting at 28° and having a sp. gr. 1·055 at 28°; the *ethyl* ester boils at 269—271° and has a sp. gr. 1·041 at 19°; the anilide (compare Henrich and Wirth, this vol., i, 431) melts at 121°. M. A. W.

Conversion of Cinnamylidenepyruvic Acid into δ-Benzylidenelævulic Acid. Emil Erlenmeyer, jun. (*Ber.*, 1904, 37, 1318—1322).—The reduction of cinnamylformic acid to α-hydroxy-γ-phenyl*iso*crotonic acid (Abstr., 1903, i, 698) is remarkable, since other similar acids undergo reduction at the double linking. Cinnamylidenepyruvic acid behaves like cinnamylformic acid.

Cinnamylidenepyruvic acid, CHPh:CH·CH:CH·CO·CO_2H, prepared by condensing pyruvic acid and cinnamaldehyde with sodium hydroxide, crystallises from water in orange needles containing H_2O and melts at 75°; it becomes yellow on drying in a vacuum and then melts at 107°. Sodium amalgam and glacial acetic acid reduce its alcoholic solution to *α-hydroxy-β-cinnamylidenepropionic acid*,

CHPh:CH·CH:CH·CH(OH)·CO_2H,

crystallising from benzene in yellow needles and melting at 145°. Boiling with dilute hydrochloric acid converts it into δ-benzylidenelævulic acid (Erdmann, Abstr., 1890, 495). C. H. D.

Preparation of Indigotin. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 149638).—The leuco-compounds obtained by fusing phenylglycine and its derivatives with alkali amides (D.R.-P. 137955) are only imperfectly oxidised to indigo dyes on dissolving in water and passing a current of air, a considerable part being always converted into red dyes, which are partially soluble in dilute acids. If sodium nitrate is added to the solution (25 kilos. to the mass obtained from 300 kilos. of phenylglycine salt), the oxidation to indigotin or its derivatives is practically complete. C. H. D.

Preparation of Bromoindigotin. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 149941 and 149989).—The action of bromine on a 10 or 20 per cent. indigo paste produces very little bromoindigotin, only bromoisatin and other decomposition products being obtained. The action of liquid or gaseous bromine on indigotin which is only moistened with water, however, yields bromoindigotin. A similar product is obtained by the bromination of indigotin in presence of concentrated hydrochloric or hydrobromic acid, with or without the addition of a carrier, such as ferrous chloride. The hydrobromic acid produced may be utilised by adding hypochlorites, &c., thus rendering the bromine again available. It has not been determined whether the products are identical with the bromoindigotins prepared synthetically from indoxyl. C. H. D.

Cork. I and II. Max von Schmidt (*Monatsh.*, 1904, 25, 277—301, 302—310).—Kügler's formula, $C_{22}H_{42}O_3$, for phellonic acid is to be preferred to Gilson's, $C_{22}H_{44}O_3$ (Abstr., 1891, 465). When boiled with acetic anhydride, phellonic acid yields an acetyl derivative, $C_{22}H_{41}O_3Ac$, which melts at 80°. With hydriodic acid, phellonic acid yields *iodophellanic acid*, $C_{22}H_{41}O_2I$, which, again, by boiling potassium hydroxide solution, is converted into phellonic acid. When treated with zinc and alcoholic hydrochloric acid, iodophellanic acid yields *ethyl* iso*phellonate*, $C_{22}H_{41}O_3Et$, which melts at 52—53° and is hydrolysed by alcoholic potassium hydroxide, forming iso*phellonic acid*, $C_{22}H_{42}O_3$. This melts at 73° and forms a soluble *potassium* salt. When heated with hydriodic acid and phosphorus, phellonic acid yields a soft, waxy *substance*, forming granular masses and melting at about 200°.

With bromine, phellonic acid forms a white, crystalline *substance*, which melts at 80—81° and loses bromine when boiled with aqueous potassium hydroxide.

Fusion of phellonic acid with potassium hydroxide leads to the formation of *phellogenic acid*, $C_{21}H_{40}O_4$, which crystallises in slender needles and melts at 121°. This dibasic acid is also obtained by fusing cork meal with potassium hydroxide. iso*Phellogenic acid* is formed from phellonic acid by the action of warm concentrated nitric acid and acetic acid. It is crystalline and melts at 100°. The action of nitric acid alone on phellonic acid and on *iso*phellogenic acid leads to the formation of suberic acid.

Gilson's violet iodine reaction and the violet coloration of cork by potassium hydroxide solution are not reactions for phellonic acid.

The following constitutional formulæ are suggested: phellonic acid, $\begin{matrix} CH_2\cdot CH(C_7H_{15})\cdot CH\cdot CO_2H \\ | \qquad\qquad\qquad\quad | \\ CH_2\cdot CH(C_7H_{15})\cdot CMe\cdot OH \end{matrix}$, phellogenic acid,

$$CO_2H\cdot CH(C_7H_{15})\cdot CH_2\cdot CH_2\cdot CH(C_7H_{15})\cdot CH_2\cdot CO_2H,$$

*iso*phellogenic acid, $C_7H_{15}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(C_7H_{15})\cdot CH(CO_2H)_2$.

The chloroform extract of cork contains glycerides of fatty acids, cerin, and other substances, but the alcoholic potassium hydroxide extract, contrary to Kügler's statement, contains at most only traces of glycerides. G. Y.

Constitution of Orsellinic Acid. Ferdinand Henrich [and, in part, with Karl Dorschky] (*Ber.*, 1904, 37, 1406—1415).—Benzenediazonium chloride (2 mols.) reacts with an alkaline solution of ethyl orsellinate yielding the *disazobenzene* derivative,

$$C_6Me(OH)_2(N_2Ph)_2\cdot CO_2Et,$$

which crystallises from acetic acid in dark red needles containing 1 mol. of acetic acid, which they lose at 130°. It melts at 186°, has basic properties, and on reduction in alcoholic solution with stannous chloride and hydrochloric acid and further heating with hydrochloric acid at 160° yields a *diamino-orcinol hydrochloride*, identical with that obtained by the reduction of dinitroso-orcinol,

$$C_6HMe(OH)_2(NO)_2\ [Me:(NO)_2:(OH)_2 = 1:2:4:3:5]$$

(compare Kostanecki, Abstr., 1888, 263).

The constitution of orsellinic acid is thus

$$C_6H_2Me(OH)_2{\cdot}CO_2H\ [Me:(OH)_2:CO_2H = 1:3:5:6];$$

the dissociation constant, $K = 0{\cdot}0127$, is in perfect harmony with this constitution.

Benzenediazonium chloride reacts with an alkaline solution of para-orsellinic acid yielding a brown product, which, on reduction, yields the isomeric 2 : 6-diamino-orcinol, which differs from the 2 : 4 compound in its colour reactions.

	2 : 4-Diamino-hydrochloride.	2 : 6-Diamino hydrochloride.
Ferric chloride	blue colour	red
Sodium hydroxide...	pale violet	yellowish-red
Dichromate	intense blue	red
Sodium nitrite	blue	brown and then dark green
Bleaching powder ...	blue, unstable.	precipitate, stable.

J. J. S.

Derivatives of Ethyl Amino orsellinate. Contribution to Formation of Litmus Dyes. FERDINAND HENRICH and KARL DORSCHKY (*Ber.*, 1904, **37**, 1416—1424).—Ethyl orsellinate in alkaline solution reacts with benzenediazonium chloride (1 mol.) yielding *ethyl benzeneazo-orsellinate*, $C_6H_5{\cdot}N_2{\cdot}C_6HMe(OH)_2{\cdot}CO_2Et$, in the form of dark orange-yellow needles melting at 142°, and soluble in alkalis and in concentrated sulphuric acid. On reduction with stannous chloride and hydrochloric acid in alcoholic suspension, it yields *ethyl amino orsellinate hydrochloride* in the form of long, colourless needles decomposing at 236°. Its *tribenzoyl* derivative crystallises in small needles melting at 222·5° and is soluble in warm benzene, ethyl acetate, or acetone.

When heated with concentrated hydrochloric acid at 160°, the ethyl ester of the amino-acid is converted into β-amino-orcinol hydrochloride (Abstr., 1903, i, 413) and must therefore have the constitution $[CH_3:CO_2Et:(OH)_2:NH_2 = 1:2:3:5:6]$.

An alkaline solution of the ethyl ester of the amino-acid is oxidised by the atmospheric oxygen to an orange-coloured dye melting at 191—192°. Its solutions in alcohol, in ethyl acetate, or acetone fluoresce, but not the solutions in benzene, light petroleum, or carbon disulphide. It has basic properties.

Benzenediazonium chloride reacts with an alkaline solution of orsellinic acid yielding *benzeneazo-orsellinic acid*,

$$C_6H_5{\cdot}N_2{\cdot}C_6HMe(OH)_2{\cdot}CO_2H;$$

this decomposes at 191° and on reduction yields β-amino-orcinol.

p-Orsellinic acid and benzenediazonium chloride yield an *azo-compound*, $C_{14}H_{12}O_4N_2$, which crystallises from nitrobenzene in long, orange-yellow needles decomposing at 191°. It is far less soluble than its isomeride in the majority of solvents, and on reduction yields the *hydrochloride* of *amino*-p-*orsellinic acid* in the form of colourless needles. J. J. S.

Action of Organo-magnesium Compounds on Phthalimide and Phenylphthalimide. CONSTANTIN BÉIS (*Compt. rend.*, 1904, 138, 987—989. Compare this vol., i, 15).—Phthalimide reacts with organo-magnesium compounds to yield derivatives of *iso*indole (*isoindolones*) according to the equations:

$$(1)\quad C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NH + 2MgEtBr =$$

$$C_6H_4{<}\genfrac{}{}{0pt}{}{\text{——}CO\text{——}}{CEt(OMgBr)}{>}NMgBr + C_2H_6;$$

$$(2)\quad C_6H_4{<}\genfrac{}{}{0pt}{}{\text{——}CO\text{——}}{CEt(OMgBr)}{>}NMgBr + H_2O = C_6H_4{<}\genfrac{}{}{0pt}{}{CO\text{-}}{CEt}{\geqslant}N \text{ or}$$

$$C_6H_4{<}\genfrac{}{}{0pt}{}{\text{——}CO\text{——}}{C(CHMe)}{>}NH + MgBr_2 + Mg(OH)_2.$$

These compounds are crystalline, almost insoluble in water, soluble in the ordinary organic solvents, and crystallise well from acetic acid; *ethyl*iso*indolone* melts at 210°, iso*butyl*iso*indolone* at 180°, and iso*amyl*iso*indolone* at 115°.

The reasons for assigning the above constitution to these compounds and not that of the isomeric ketonitrile, $CN\cdot C_6H_4\cdot CO\cdot R$, are (1) the compounds give neither semicarbazones, phenylhydrazones, nor any colour reactions of ketones; (2) they are not reduced by sodium in alcoholic solution, or by zinc and acetic acid; (3) they do not give acids on boiling with alcoholic potassium hydroxide; (4) the melting point of ethyl*iso*indolone is 210°, much higher than that of the corresponding acid, $CO_2H\cdot C_6H_4\cdot COEt$, which melts at 91°, whereas the nitrile usually has a lower melting point than the acid.

M. A. W.

Configuration of the Stereoisomeric Phenylmethylitaconic Acids. (Indoneacetic Acids. II.) HANS STOBBE [and, in part, ROBERT ROSE] (*Ber.*, 1904, 37, 1619—1624. Compare Abstr., 1902, i, 542).—Concentrated sulphuric acid at 0° converts phenylmethyl*iso*-itaconic acid (melting at 183°) into a mixture of methylindoneacetic acid and hydroxymethylhydrindoneacetolactone.

3-*Methyl*-1-*indone*-2-*acetic acid*, $C_6H_4{<}\genfrac{}{}{0pt}{}{CMe}{\text{-}CO\text{-}}{\geqslant}C\cdot CH_2\cdot CO_2H$, crystallises from benzene in small, yellow prisms, melts at 154—155°, and dissolves readily in alcohol, ether, chloroform, or acetic acid, more sparingly in benzene or light petroleum, very sparingly in water. It forms yellow alkali salts and dissolves in concentrated sulphuric acid to a violet solution, slowly becoming colourless. The *semicarbazone*, $C_{13}H_{13}O_3N_3$, forms bright yellow needles and melts and decomposes at 218—219°. Potassium permanganate oxidises the acid to phthalic acid.

The *lactone* of 3-*hydroxy*-3-*methyl*-1-*hydrindone*-2-*acetic acid*,

$$\begin{array}{l} C_6H_4\cdot CMe\text{—}O \\ CO\text{—}CH\cdot CH_2 \end{array}{>}CO,$$

forms colourless, rhombic crystals, melts at 179·5°, and dissolves

sparingly in ether, more readily in alcohol or acetone. Bases form the yellow salts of methylindoneacetic acid, not the colourless salts of the hydroxy-acid. The *semicarbazone*, $C_{13}H_{13}O_3N_3$, forms white needles and melts and decomposes at 258—259°.

Phenylmethylitaconic acid, on treatment with cold concentrated sulphuric acid, yields phenylmethylitaconic anhydride only. The diethyl ester yields a mixture of the acid and anhydride.

The results prove that γ-phenyl-γ-methyl*iso*itaconic acid, melting at 183°, is the *cis*-modification, $\begin{matrix}Ph\cdot C\cdot Me\\ \Vert\\ CO_2H\cdot C\cdot CH_2\cdot CO_2H\end{matrix}$, and γ-phenyl-γ-methylitaconic acid, melting at 171°, is the *cis-trans*-modification, $\begin{matrix}Ph\cdot C\cdot Me\\ \Vert\\ CO_2H\cdot CH_2\cdot C\cdot CO_2H\end{matrix}$.

C. H. D.

General Method for Preparing Substituted Malonic Acids. GALEAZZO PICCININI (*Atti R. Accad. Sci. Torino*, 1904, **39**, 121—139).—Aldehydes condense with cyanoacetamide according to the equation

$$R\cdot CHO + CN\cdot CH_2\cdot CO\cdot NH_2 + H_2 = R\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2 + H_2O,$$

the hydrogen on the left hand side of the equation being supplied by the reacting substances; on hydrolysis, the resultant amide produces the acid $R\cdot CH_2\cdot CH(CO_2H)_2$.

Methylenedioxybenzylmalonic acid, $CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH_2\cdot CH(CO_2H)_2$, prepared by hydrolysing with baryta water the amide,

$$CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2,$$

formed from the interaction of piperonaldehyde with ethyl cyanoacetate and ammonia, crystallises from water in hard, lustrous prisms and melts at 142—144°; the *barium* salt, $C_{11}H_8O_6Ba,3H_2O$, and the *calcium* salt, $C_{11}H_8O_6Ca,\frac{1}{2}H_2O$, are crystalline. On heating the acid for several hours at 130°, it evolves carbon dioxide and is converted into methylenehydrocaffeic acid, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot CO_2H$ (Lorenz, Abstr., 1881, 49). If the foregoing amide is hydrolysed with milk of lime instead of with baryta, *methylenedioxybenzylcyanoacetic acid*, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH(CN)\cdot CO_2H$, is obtained; it crystallises from ether in colourless needles or prisms and melts at 142°.

iso*Amylmalonic acid*, $CH_2Pr^{\beta}\cdot CH_2\cdot CH_2\cdot CH(CO_2H)_2$, is prepared by hydrolysing *iso*amylcyanoacetamide, obtained by the interaction of *iso*valeraldehyde with ethyl cyanoacetate or cyanoacetamide in presence of ammonia; it separates from ether in small, hard crystals and melts at 98°.

n-*Heptylmalonic acid*, $CH_3\cdot[CH_2]_6\cdot CH(CO_2H)_2$, prepared by hydrolysing *n*-heptylcyanoacetamide with baryta water, separates from benzene in lustrous, unctuous crystals, melts at 95°, and gives a micro-crystalline *barium* salt, $C_{10}H_{16}O_4Ba,3H_2O$. n-*Heptylcyanoacetic acid*, $CH_3[CH_2]_6\cdot CH(CN)\cdot CO_2H$, is formed simultaneously in small quantity; it crystallises from ether and melts at 141°.

Attempts to hydrolyse piperonylcyanoacetamide,

$$CH_2{:}O_2{:}C_6H_3\cdot CH{:}C(CN)\cdot CO\cdot NH_2,$$

with aqueous barium hydroxide gave only piperonaldehyde and malonic acid, not piperonylmalonic acid, $CH_2{:}O_2{:}C_6H_3\cdot CH{:}C(CO_2H)_2$;

the latter compound also could not be obtained by condensing together malonic acid and piperonaldehyde in presence of glacial acetic acid, piperonylacrylic acid being the sole product (compare Lorenz, *loc. cit.*).

W. A. D.

Polymeric Coumaric Acids. KNUT T. STRÖM (*Ber.*, 1904, 37, 1383—1386).—*o*-Coumaric acid and its alkyl derivatives polymerise on exposure to light, the original crystals falling to powder.

Bis-o-*coumaric acid*, $C_{18}H_{16}O_6$, crystallises from water and melts above 275°, decomposing at higher temperatures into coumarin and a compound not yet identified, which sublimes in leaflets. Boiling glacial acetic acid converts the acid into *biscoumarin*, which crystallises in small needles or leaflets and does not melt at 275°. It does not appear to be identical with Ciamician and Silber's polymeric coumarin (Abstr., 1903, i, 171).

Bisethyl-o-*coumaric acid* melts at 273—274°, *bispropyl*-o-*coumaric acid* at 254°, *bisisopropyl*-o-*coumaric acid* at 264°, and *bisallyl*-o-*coumaric acid* at 236°. The polymerisation of α-propylcoumaric acid was complete in 3 days, whilst the β-acid required 14 days. No polymerisation occurs in alcoholic solution.

The polymeric acids are dibasic; they form calcium salts containing $5H_2O$, and esters which crystallise in needles. The alkyl acids are not altered by boiling with acetic acid, being unable to form a double lactone corresponding with biscoumarin.

C. H. D.

Digitogenic Acid and its Decomposition Products. HEINRICH KILIANI and J. SCHWEISSINGER (*Ber.*, 1904, 37, 1215—1221).—Digitogenic acid, prepared by Kiliani and Merk's method (Abstr., 1902, i, 46), melts at 210°, whereas when prepared by the older method it melts at 155°; it is shown that this is due to glacial acetic acid being used as the solvent, as this converts the substance melting at 155° into the less fusible form. The two modifications give the same analytical results, and apparently the same magnesium salt; by boiling the form melting at 210° with alcohol, it is partially reconverted into that melting at 155°.

Digitic acid may be prepared by oxidising either of these modifications of digitogenic acid with alkaline potassium permanganate solution; details are given of its preparation and of that of its acid potassium salt, which is sparingly soluble in water, crystallises from 50 per cent. alcohol in nacreous leaflets, and melts at 235°. Analyses of the salt agree with either of the formulæ

$$C_{40}H_{63}O_{16}K\ (=C_{20}H_{31}O_8K,C_{20}H_{32}O_8)$$

or $C_{38}H_{61}O_{15}K$. The first explains the fact that when the salt is dissolved in boiling water, slender needles, apparently of digitic acid ($C_{20}H_{32}O_8$?), separate; on the other hand, barium digitate (Kiliani, Abstr., 1891, 577), which was formerly considered to be

$$C_{20}H_{30}O_8Ba,6H_2O,$$

gives numbers agreeing more closely with the formula

$$C_{38}H_{58}O_{15}Ba_2,12H_2O.$$

Anhydrodigitic acid (Kiliani and Baylen, Abstr., 1895, i, 65), on

titration with phenolphthalein as indicator, gives an equivalent 241. This does not agree with the previous formula, $C_{20}H_{28}O_6$, and analyses of the purified calcium salt are equally discordant. It appears that anhydrodigitic acid is probably a mixture of acids; when it is fractionally precipitated from acetone by adding water, the less soluble material *A* gives, with magnesium nitrate in aqueous solution, an insoluble salt, whereas the more soluble acid *B* is not so precipitated. The fraction *A* has a mol. wt. 475, and fraction *B* a mol. wt. 489.

W. A. D.

p-Halogen-*o*-nitrobenzaldehydes. FRANZ SACHS (D.R.-P., 149748 and 149749).—*o*-Nitro-*p*-aminobenzaldoxime (Abstr., 1902, i, 377) is readily converted into *p*-halogen-*o*-nitrobenzaldehyde by boiling with haloid acids and a ferric salt. The hydroxylamine at first formed is probably oxidised by the ferric salt to nitrous acid, which then diazotises the amino-group. The oxime may also be converted into halogen derivatives by diazotising and boiling with a haloid acid and a cuprous salt.

p-*Chloro*-o-*nitrobenzaldehyde phenylhydrazone* melts at 176—177° and the *semicarbazone* at 269—270°. p-*Bromo*-o-*nitrobenzaldehyde*, $C_7H_4O_3NBr$, melts at 97—98° and its *phenylhydrazone* at 181—182°. p-*Iodo*-o-*nitrobenzaldehyde* melts at 110—111° and its phenylhydrazone at 185°.

C. H. D.

p-Dimethylaminobenzaldehyde. II. FRANZ SACHS and PAUL STEINERT (*Ber.*, 1904, 37, 1733—1745. Compare Abstr., 1903, i, 37).—*p*-Dimethylaminobenzaldehyde can be purified by distillation at 176—177° under 17 mm. pressure.

Hexamethyltriaminohydrobenzamide, $N_2(CH{\cdot}C_6H_4{\cdot}NMe_2)_3$, formed by the action of alcoholic ammonia on dimethylaminobenzaldehyde, crystallises in colourless prisms, melts at 193°, is easily soluble in chloroform, less so in alcohol, and is insoluble in ether or light petroleum. In glacial acetic acid or acetic anhydride, it dissolves to a dark green solution, which becomes bluish-green on warming. The *hydrochloride*, $C_{27}H_{33}N_5,3HCl$, melts at 264—265°; the *picrate*, $C_{27}H_{33}N_5,C_6H_3O_7N_3$, assumes a green colour at 160—170°, and melts at 213°; the *oxalate* melts at about 140—145°. When heated for 6 hours at 150—160°, hexamethyltriaminohydrobenzamide forms hexamethyltriaminocyaphenine and octomethyltetraminotetraphenylpyrazine.

Hexamethyltriaminocyaphenine,

$$NMe_2{\cdot}C_6H_4{\cdot}C{<}{\begin{matrix}N{:}C(C_6H_4{\cdot}NMe_2)\\N{\cdot}C(C_6H_4{\cdot}NMe_2)\end{matrix}}{>}N,$$

forms trimetric crystals, melts at 357° (corr.), and is insoluble in acetone. Octomethyltetraminotetraphenylpyrazine,

$$\begin{matrix}NMe_2{\cdot}C_6H_4{\cdot}\underset{|}{C}H{\cdot}\underset{|}{N}{\cdot}\underset{|}{C}H{\cdot}C_6H_4{\cdot}NMe_2\\NMe_2{\cdot}C_6H_4{\cdot}CH{\cdot}N{\cdot}CH{\cdot}C_6H_4{\cdot}NMe_2\end{matrix},$$

is precipitated from its alcoholic solution by aqueous ammonia as a voluminous, yellow precipitate, melts at 95°, is soluble in acetone, and with bromine in alcoholic solution yields octomethyltetraminotetraphenyldibromopiperazine, which is dark red, melts at 95°, and loses its bromine when boiled with alcohol.

The *oxime* of *p*-dimethylaminobenzaldehyde melts at 144°. When boiled with acetic anhydride, it yields *p*-dimethylaminobenzonitrile, which boils without decomposition at 318° (corr.) under 758 mm. pressure and is volatile with steam.

p-*Dimethylamino*-m-*nitrobenzamide*, prepared by treating the nitrile with nitric and sulphuric acid, crystallises from water and melts at 210°.

p-*Nitrosomethylaminobenzonitrile*, formed by the action of sodium nitrite and hydrochloric acid on *p*-dimethylaminobenzonitrile, has a yellow colour, crystallises from water, melts at 125°, and gives Liebermann's nitroso-reaction. When boiled with hydrochloric acid and stannous chloride, it yields p-*methylaminobenzonitrile*, which forms white crystals and melts at 85—86°.

With magnesium phenyl bromide, *p*-dimethylaminobenzaldehyde forms *p*-dimethylaminodiphenylcarbinol; with magnesium ethyl bromide, it forms p-*dimethylaminophenylpropylene*,

$$NMe_2{\cdot}C_6H_4{\cdot}CH{:}CHMe,$$

which melts at 48°.

The action of *p*-dimethylaminobenzaldehyde on pyruvic acid and β-naphthylamine leads to the formation of 3-*p*-dimethylaminophenyl-β-naphthacinchonic acid, $C_{10}H_6{<}\begin{matrix}N{=\!=\!=}C{\cdot}C_6H_4{\cdot}NMe_2\\ C(CO_2H){:}CH\end{matrix}$, which melts at 293—295°, and at 300—310° loses carbon dioxide, yielding 3-*p*-dimethylaminophenyl-β-naphthaquinoline,

$$C_{10}H_6{<}\begin{matrix}N{=}C{\cdot}C_6H_4{\cdot}NMe_2\\ CH{:}CH\end{matrix}.$$

This crystallises in brown needles, melts at 245°, and is insoluble in most solvents. *Dinitro*-3-p-*dimethylaminophenyl*-β-*naphthacinchonic acid*, formed by nitration of the acid, melts at 260—263°.

p-*Dimethylaminobenzylideneacetylacetone*, prepared by acting with the aldehyde on acetylacetone in presence of piperidine, crystallises in yellow needles and melts at 95°. p-*Dimethylaminobenzylidenebenzoylacetone*, $NMe_2{\cdot}C_6H_4{\cdot}CH{:}CAc{\cdot}COPh$, crystallises in yellow, monoclinic prisms, melts at 184°, dissolves in concentrated sulphuric acid to a yellow solution, and dyes wool yellow in acetic acid solution.

2′ : 4′-Dinitro-4-dimethylaminostilbene,

$$NMe_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_3(NO_2)_2,$$

obtained from *p*-dimethylaminobenzaldehyde and 2 : 4-dinitrotoluene, crystallises in long needles, melts at 181°, dissolves in concentrated sulphuric acid to a yellow and in glacial acetic acid to a dark red solution; in acetic acid solution it dyes wool reddish-brown. 2 : 6-Dinitrotoluene and *p*-dimethylaminobenzaldehyde form a *condensation product*. 2 : 4 : 6-Trinitrotoluene and *p*-dimethylaminobenzaldehyde form an *additive* compound, $C_9H_{11}ON,C_7H_5O_6N_3$, which melts at 60° and is decomposed by mineral acids. G. Y.

[Action of Formaldehyde and Lime on Cinnamaldehyde.] BERNHARD TOLLENS (*Ber.*, 1904, **37**, 1435. Compare Marle and Tollens, Abstr., 1903, i, 493).—The products obtained by the action of formaldehyde and ammonium chloride are the *hydrochlorides* of bases

and not monomethylolacetophenone and trimethylolbisacetophenone. The *bases* are only slightly soluble in water and yield *platinichlorides*. The oil, previously described as phenyl vinyl ketone, is obtained when the hydrochlorides are distilled in steam, and is free from chlorine.

G. Y.

Condensations of Piperonylacraldehyde and of Piperonal.

MAX SCHOLTZ and F. KIPKE (*Ber.*, 1904, 37, 1699—1704. Compare Abstr., 1895, i, 42, 464, 468).—With the three toluidines, piperonylacraldehyde forms an o-*toluidide*, which crystallises in long needles and melts at 94—95°, a m-*toluidide*, which crystallises in strongly refracting leaflets and melts at 95°, and a p-*toluidide*, which crystallises in leaflets and melts at 138°.

With acetylacetone, piperonylacraldehyde condenses in absolute alcoholic solution in presence of piperidine, with formation of *piperonyleneacetylacetone*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CAc_2$, which crystallises in yellow needles, melts at 105°, gives a deep violet coloration with concentrated sulphuric acid, and forms a *phenylhydrazone*; this crystallises in yellow needles and melts at 160—161°. In presence of an alkali, piperonylacraldehyde condenses with *p*-tolyl methyl ketone to form p-*tolyl piperonylenemethyl ketone*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}C_7H_7,$$

which crystallises in yellow needles, melts at 122°, and gives a deep violet coloration with concentrated sulphuric acid.

The *semicarbazone* of piperonylacraldehyde,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

crystallises from pyridine in colourless leaflets and melts at 226°. At 227—230°, it is converted into 1-*carbamido*-5-*piperonyl*-4 : 5-*pyrazoline* (compare Scholtz, Abstr., 1896, i, 343; Harries, Abstr., 1899, i, 637), which forms a *picrate* and a hydrochloride. The *uranium tetrachloride* double salt, $C_{11}H_{11}O_3N_3(UCl_4)_2$, was the only pure product obtained. The *oxime* of piperonyleneacetone melts at 176°. At high temperatures, it loses water and yields a small amount of a *base*, which crystallises in leaflets and forms a *mercurichloride* melting at 186°.

Piperonal condenses with naphthyl methyl ketone less easily than with *p*-tolyl methyl ketone. The *product* forms yellow, granular crystals and melts at 141°. The condensation *product*, $C_{18}H_{13}O_2N$, of piperonal and *β*-naphthylamine crystallises from alcohol in leaflets containing 1 mol. C_2H_6O, and melts at 115°.

The action of piperonal on *o*-phenylenediamine, in alcoholic solution leads to the formation of the *aldehydine* base,

$$\begin{array}{l} C_6H_4{\cdot}N{\cdot}CH_2{\cdot}C_6H_3{:}O_2{:}CH_2 \\ N\text{——}C{\cdot}C_6H_3{:}O_2{:}CH_2 \end{array},$$

which forms yellow, granular crystals containing 1 mol. C_2H_6O, melts at 115—116°, and forms a *hydrochloride* melting at 277°.

Ethyl piperonylacetoacetate, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CAc{\cdot}CO_2Et$, formed by the action of piperonal on ethyl acetoacetate in presence of piperidine, melts at 83° and forms a *phenylhydrazone* which crystallises in yellow leaflets and melts at 135°.

G. Y.

Syntheses of Bridged Dicyclic Systems. II. Addition o Ethyl Acetoacetate to Carvone. Paul Rabe and Karl Weilinger (*Ber.*, 1904, **37**, 1667—1671. Compare Abstr., 1903, i, 268, 269).—Ethyl chlorotetrahydrocarvonylacetoacetate reacts with zinc dust, glacial acetic acid, and concentrated hydrochloric acid yielding a mixture of *ethyl dihydrocarvonylacetoacetate*,

$$CO_2Et\cdot CHAc\cdot CH{<}\begin{matrix}CH_2\cdot CH(CMe{:}CH_2)\\ CHMe\text{————————}CO\end{matrix}{>}CH_2,$$

and *ethyl* 8-*acetoxyterpan*-2-*one*-6-*ylacetoacetate*,

$$CO_2Et\cdot CHAc\cdot CH{<}\begin{matrix}CH_2\cdot CH(CMe_2OAc)\\ CHMe\text{————————}CO\end{matrix}{>}CH_2.$$

The acetate crystallises from alcohol in six-sided, prismatic needles melting at 133°. It is the ketonic form, and by means of the sodio-derivative may be converted into the enolic form, which gives a purple coloration with ferric chloride.

The dihydro-ester is a colourless oil, gives a reddish-violet coloration with alcoholic ferric chloride, and readily decolorises alkaline permanganate. On reduction with sodium and alcohol, it yields iso*propenylmethyldicyclononanolone* in the form of an oil distilling at 175—185° under 15 mm. pressure, and on further reduction yields the solid glycol melting at 172—173° (Abstr., 1903, i, 268). Both liquid and solid glycols, on reduction with phosphorus and hydriodic acid, yield 3-iso*propyl*-9-*methyldicyclononane*,

$$CH_2{<}\begin{matrix}CH_2\cdot CH-CH_2-\\ \qquad\qquad {>}CHMe\ {>}CH\cdot CHMe_2.\\ CH_2\cdot CH-CH_2-\end{matrix}$$

It is a colourless liquid, which distils at 132° under 28 mm. pressure, or at 232—233° under 755 mm., has a sp. gr. 0·8643 at 20°/4°, n_D 1·4660 at 20°, and is optically inactive. J. J. S.

Syntheses of Bridged Dicyclic Systems. III. Addition of Ethyl Acetoacetate to Methylcyclohexenone. Paul Rabe (*Ber.*, 1904, **37**, 1671—1674. Compare Abstr., 1903, i, 268, and preceding abstract).—3-Methylcyclo-Δ^2-hexen-1-one (Hagemann, Abstr., 1893, i, 393; Knoevenagel, *ibid.*, 1895, i, 51) is obtained when ethyl methylcyclohexanoldicarboxylic acid (*Annalen*, 1904, **332**, 1) is boiled with 10 per cent. sulphuric acid neutralised with ammonia and saturated with ammonium sulphate. The ketone is miscible with water in all proportions and condenses with ethyl acetoacetate in the presence of sodium ethoxide solution, yielding *methyl dicyclononanolone*,

$$CO{<}\begin{matrix}CH_2-CMe-CH_2\\ \qquad\qquad {>}CH_2\ {>}CH_2,\\ CH_2\cdot C(OH)-CH_2\end{matrix}$$

as a thick, yellow oil, which distils at 170—173° under 17—18 mm. pressure, and on cooling partially solidifies. The *acetate* is an oil distilling at 172—176° under 16 mm. pressure. On reduction with sodium and alcohol, the ketoalcohol yields 1-*methyldicyclononane*-5 : 7-*diol*, which crystallises from ether in colourless plates melting at 124—125°, and yielding a *diacetate* in the form of a thick oil. 1-*Methyl-dicyclononane*, obtained by reducing the glycol with phosphorus and hydriodic acid, is a colourless liquid distilling

at 176—178° under 751 mm. pressure; it has a sp. gr. 0·8416 at 20°/4° and n_D 1·4529 at 20°. J. J. S.

Preparation of Dibenzyl Ketone. HERMANN APITZSCH (*Ber.*, 1904, **37**, 1428—1429. Compare Stobbe, *Annalen*, 1899, **308**, 175; Young, Trans., 1891, **59**, 625; H. Wieland, this vol., i, 432).—Calcium phenylacetate is dried for an hour in flat porcelain dishes at 150—160°. The roughly powdered salt is heated in a non-tubulated retort of Jena glass over a Teclu burner. The distillate is dissolved in ether, dried with sodium sulphate, and fractionated. The yield of ketone, boiling at 324—325° under 739 mm. pressure, is 83 per cent. J. J. S.

Action of Carbon Disulphide and Potassium Hydroxide on Dibenzyl Ketone. HERMANN APITZSCH [and F. METZGER] (*Ber.*, 1904, **37**, 1599—1610).—When dibenzyl ketone (preceding abstract) is boiled with carbon disulphide and solid potassium hydroxide, a compound insoluble in alkalis is obtained, and acids precipitate an orange compound of the formula $C_{18}H_{12}OS_3$, crystallising from chloroform in large, ruby-red crystals containing $CHCl_3$ and melting at 165°. It dissolves readily in ether, benzene, or ethyl acetate, and separates in each case with 1 mol. of solvent of crystallisation. The *sodium* derivative, $C_{18}H_{10}OS_3Na_2$, forms yellow, readily soluble needles containing $2C_2H_5{\cdot}OH$; the *potassium* (containing $12H_2O$), *ammonium*, and *barium* (with $10H_2O$) derivatives are described.

The *diethyl ether*, $C_{18}H_{10}OS_3Et_2$, forms characteristic, saw-blade like crystals and melts at 141·5—142°. The *dibenzyl ether* crystallises from benzene and melts at 131°. The *dipropyl ether* forms almost colourless, glistening crystals and melts at 88°; the *dimethyl ether* forms white crystals and melts at 167°. The ethers are only slowly hydrolysed by heating with alcoholic hydrogen chloride or potassium hydroxide at 300°. The *dibenzoyl ester* forms yellow needles and melts at 142°.

Solutions of the acid compound in indifferent solvents decompose on exposure to light, forming a crystalline complex *anhydride*. Zinc and hydrochloric acid remove 2 atoms of sulphur from the acid compound, forming a *compound*, $C_{18}H_{16}OS$, crystallising from alcohol in colourless needles melting at 136·5° and having no acid properties.

The orange acid compound is probably 1-*keto*-2 : 6-*diphenyl*-4-*thiophen*-3 : 5-*dithiol*, $CS{<}{\substack{C(SH){:}CPh \\ C(SH){:}CPh}}{>}CO$, yielding

$$CS{<}{\substack{CH_2{\cdot}CHPh \\ CH_2{\cdot}CHPh}}{>}CO$$

on reduction.

Diethyl ketone yields a similar orange compound, which will be further investigated. C. H. D.

Reduction of Ketones. H. APITZSCH and F. METZGER (*Ber.*, 1904, **37**, 1676—1679).—A theoretical yield of hydrobenzoin (m. p. 134°) may be obtained by the reduction of benzoin with stannous chloride in the presence of alcoholic hydrogen chloride. Anisoin, when reduced in a similar manner, yields iso*hydroanisoin*

melting at 109°, but cuminoin cannot be reduced by a similar process. Methyl- and ethyl-benzoins (Fischer, Abstr., 1894, i, 38) and benzoin-anilide are not reduced even in sealed tubes at 120°, but at 140° they are decomposed yielding benzoin, which is then reduced.

Benzil with an excess of stannous chloride is quantitatively reduced to hydrobenzoin, and anisil to *iso*hydroanisoin.

Acetophenone, benzophenone, deoxybenzoin, dibenzyl ketone, benzylacetophenone, and benzylideneacetophenone could not be reduced. Acetone yields methyl and *iso*propyl alcohols and mesityl oxide. Benzoquinone and phenanthraquinone are reduced to the corresponding quinols, but anthraquinone is not affected. J. J. S.

Decomposition of Methiodides in Acid Solution. Paul Rabe and William Denham (*Ber.*, 1904, 37, 1674—1675).—When cinchonine methiodide is warmed in dilute acetic acid solution for 72 hours, the ring is ruptured and methylcinchotoxin is formed (Claus and Müller, Abstr., 1880, 289; 1895, i, 435). The reaction is similar to the rupture of bridged rings previously observed in alkaline solution (Claus and Müller, *loc. cit.*; Freund and Rosenstein, *ibid.*, 1894, i, 151). J. J. S.

Desmotropism of Halogen-substituted Acid Methylene Groups in the Diketohydrindene Series. Leopold Flatow (*Ber.*, 1904, 37, 1787—1790).—A theoretical discussion of the facts already published by the author (Abstr., 1901, i, 543). It is shown that in the diketohydrindene series the compound obtained by replacing hydrogen by bromine has enolic characteristics, whereas on replacing hydrogen by chlorine a compound is obtained which reacts as a ketone. E. F. A.

Quinonedi-imide. Richard Willstätter and Eugen Mayer (*Ber.*, 1904, 37, 1494—1507).—*Quinonedi-imide dihydrochloride*, obtained by the action of hydrogen chloride on quinone dichloroimide, rapidly decomposes in moist air; the salt is slightly yellow, dissolves in much water without coloration, but with small quantities of water it gives green, brown, and finally violet shades. A similar behaviour is shown by the solutions in fairly concentrated mineral acids. To obtain *quinonedi-imide* from this salt, ammonia gas is passed into the ethereal suspension of the compound, but special precautions are necessary for success to be obtained. The pure di-imide forms bright yellow, monoclinic prisms, which, on warming, decompose between 50° and 60°. It explodes on heating on the water-bath, violently when concentrated sulphuric acid is added. It yields *p*-phenylenediamine on reduction; when warmed with dilute mineral acids, quinone and ammonia are formed. The aqueous solution rapidly decomposes forming a product, which behaves similarly to Bandrowski's tetra-aminodiphenyl-*p*-azophenylene (Abstr., 1894, i, 236), which the authors find can be crystallised from nitrobenzene and aniline, and then forms green crystals with a metallic lustre, melting at 238°. E. F. A.

Oxidation Product from *p*-Tolylenediamine. JULIUS SCHMIDT and ADOLF SAAGER (*Ber.*, 1904, 37, 1679—1680. Compare Willstätter and Mayer, preceding abstract).—A *toluquinonemonoimide hydrochloride*, $O{:}C_6H_3Me{:}NH,HCl$ [O : Me : NH = 1 : 2 : 4 or 1 : 3 : 4], may be obtained by oxidising a 1 per cent. aqueous solution of *p*-tolylenediamine hydrochloride with ferric chloride at the ordinary temperature and then saturating with common salt. It crystallises from hot dilute hydrochloric acid in small, purple-black needles, and its solutions in water or alcohol are blue, but are decolorised by the addition of alkalis. J. J. S.

Preparation of Amino- and Hydroxy-anthraquinones and their Halogen Derivatives. BASLER CHEMISCHE FABRIK (D.R.-P. 148110).—Heating with sulphuric acid converts amino- and hydroxybenzoyl-*o*-benzoic acids (prepared by nitration and reduction of benzoyl-*o*-benzoic acid) almost quantitatively into amino- or hydroxyanthraquinones. The same reaction occurs with the halogen-substituted *m*-amino- and *m*-hydroxy-benzoyl-*o*-benzoic acids, which may be prepared either by condensing halogenated phthalic anhydrides with benzene or its halogen derivatives, nitrating, and reducing; or by condensing phthalic anhydride with halogenated benzenes, nitrating, and reducing.

m-*Nitrobenzoyl*-o-*benzoic acid* crystallises from acetic acid and melts at 186—187°. Iron and hydrochloric acid reduce it to m-*aminobenzoyl*-o-*benzoic acid*, melting and decomposing at 165°. The diazo-compound of the latter substance, when boiled, yields m-*hydroxybenzoyl*-o-*benzoic acid*, which melts at 181—182°. Heating with sulphuric acid converts these acids into mixtures of α- and β-amino- or hydroxyanthraquinones.

p-*Chloro*-m-*nitrobenzoyl*-o-*benzoic acid*, prepared by nitrating *p*-chlorobenzoyl-*o*-benzoic acid, crystallises from alcohol and melts at 202—204°, and on reduction yields p-*chloro*-m-*aminobenzoyl*-o-*benzoic acid*, melting at 175—176°. Heating with sulphuric acid converts the amino-acid into 3-*chloro*-2-*aminoanthraquinone*, melting at 280—283°. 3-*Chloro*-2-*hydroxyanthraquinone* forms golden-yellow needles and melts at 258—260°. 3-*Bromo*-2-*aminoanthraquinone* melts at 267—270°, and 3-*bromo*-2-*hydroxyanthraquinone* at 249—252°. C. H. D.

[1-Amino-5- and -8-hydroxyanthraquinones.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 149780).—1-Amino-5- and -8-hydroxyanthraquinones are conveniently prepared by nitrating anthraquinone-α-sulphonic acid, separating the 1 : 5- and 1 : 8-nitroanthraquinonesulphonic acids, reducing, and heating with lime under pressure (compare Wacker, Abstr., 1903, i, 132). Brown- or orange-coloured monobromo-derivatives are obtained by suspending the aminohydroxyanthraquinones in water, warming to 60°, adding bromine slowly, and heating to 100°. They dissolve sparingly in organic solvents. The condensation product from *p*-toluidine crystallises from pyridine or chlorobenzene in dark blue needles and dissolves in aniline to a greenish-blue solution. C. H. D.

4-Nitroalizarin 2-Alkyl Ethers. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 150322).—Whereas on nitration alizarin yields a mixture of nitroalizarins with nitropurpurin and purpurin, the alkyl ethers readily form well-defined nitro-compounds, the nitro-group occupying the 4-position.

4-*Nitroalizarin 2-methyl ether*, $C_6H_4<^{CO}_{CO}>C_6H(OH)(NO_2)\cdot OMe$, prepared by nitrating alizarin 2-methyl ether, crystallises from glacial acetic acid in yellow leaflets, melts at 280—282° (uncorr.), and dissolves sparingly in alcohol, ether, or benzene, readily in nitrobenzene. The alkali salts form red needles. 4-*Aminoalizarin 2-methyl ether* forms a reddish-brown powder, dissolving with difficulty in hot dilute solutions of alkali hydroxides. The solution in concentrated sulphuric acid shows a yellow fluorescence on the addition of boric acid.

The *ethyl ether* closely resembles the methyl compound.

C. H. D.

Preparation of Anthraquinone-α-sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 149801).—Anthraquinone-α-sulphonic acid is obtained in a pure state, free from β-acid or disulphonic acids, when anthraquinone is sulphonated in the presence of small quantities of mercury or mercury salts. The *potassium* salt crystallises in bright yellow, glistening leaflets, sparingly soluble in water; when heated at 180—190° with aqueous ammonia, it yields the characteristic α-aminoanthraquinone. C. H. D.

Nitro-compounds of the Menthane Series. II. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 237—246. Compare Abstr., 1900, i, 324).—Menthane is readily nitrated by nitric acid of sp. gr. 1·075 both in open and closed vessels, the main product in either case being tert.-*nitromenthane*, $C_{10}H_{19}\cdot NO_2$, which is a colourless, mobile liquid boiling at 135—137° under 25 mm. pressure, has the sp. gr. 1·0005 at 0°/0° and 0·9871 at 22°/0° and n_D 1·46241 at 22°. On reduction by means of tin and hydrochloric acid, it yields a *menthylamine*, $C_{10}H_{19}\cdot NH_2$, which boils at 199—200° under 750 mm. pressure and has the sp. gr. 0·8690 at 0°/0° and 0·8451 at 22°/0° and n_D 1·45622 at 22°. This compound is not identical with either the menthylamine or the carvomenthylamine previously described by Baeyer (Abstr., 1893, i, 722), and probably has the constitution

$$CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>CH\cdot CMe_2\cdot NH_2;$$

the *hydrochloride* melts at 140—150° and the *platinichloride* decomposes at 220°; the *benzoyl* derivative separates from light petroleum in stellate aggregates of crystals melting at 153°; the *nitrate* and *sulphate* are readily soluble in water, and the *oxalate* only slightly so.

The *benzoyl* derivative of *menthonamine*, $C_{17}H_{23}O_2N$, separates from light petroleum in white needles, which melt at 145—146° and dissolve readily in benzene, in which solvent it has $[\alpha]_D - 30·48°$. T. H. P.

Farnesol, a New Sesquiterpene Alcohol. HAARMANN & REIMER (D.R.-P. 149603).—The only sesquiterpene alcohol hitherto

known has been santalol (von Soden, Abstr., 1900, i, 677). *Farnesol*, $C_{15}H_{26}O$, a new sesquiterpene alcohol, is obtained from various acacia oils, from musk oil, and from lime-tree blossom oil, by saponifying the esters present, distilling under 200 mm. pressure, and converting the fraction boiling at 150—200° into esters by means of phthalic or other anhydride. Farnesol is a colourless oil with a fragrant odour, boiling at 160° (uncorr.) under 10 mm. pressure; it has a sp. gr. 0·885 and n_D 1·488. C. H. D.

Mechanism of the Dehydration of Menthol by Organic Acids. I. Zelikow (*Ber.*, 1904, 37, 1374—1383).—See Abstr., 1903, i, 184. C. H. D.

Campholene Derivatives. Auguste Béhal (*Bull. Soc. chim.*, 1904, 31, 461—466. Compare Abstr., 1902, i, 419, and this vol., i, 329).—*Dimethylcampholenol*, $\begin{matrix}CMe_2\cdot CMe\\ | \\ CH_2—CH_2\end{matrix}\!\!>\!C\cdot CH_2\cdot CMe_2\cdot OH$, prepared by the action of magnesium methyl iodide on methyl campholenate, boils at 110—112° under 23 mm. and at 218—220° under the atmospheric pressure, has a sp. gr. 0·9116 at 0° and 0·8996 at 16°, and n_D 1·4722 at 16°. The *acetyl* derivative, obtained by the action of acetic anhydride on the magnesium bromide derivative of the alcohol, boils at 118—122° under 19 mm. pressure, has a sp. gr. 0·9387 at 0° and 0·9266 at 16°, and n_D 1·46459.

When dimethylcampholenol is slowly distilled with acetic anhydride, it is converted principally into *dimethylcampholandiene*,

$$C_8H_{13}\cdot CH\colon CMe_2.$$

This boils at 188—190°, has sp. gr. 0·8421 at 0° and 0·8311 at 16°, and n_D 1·46707 at 16°. A mixture of this hydrocarbon with dimethylcampholene oxide is produced when dimethylcampholenol is heated with sulphuric acid.

Diethylcampholenol, prepared in an analogous manner, boils at 144—148° under 28 mm. pressure, has a sp. gr. 0·9250 at 0° and 0·9113 at 19°, and n_D 1·47730 at 19°. *Diethylcampholandiene*,

$$C_8H_{13}\cdot CH\colon CEt_2,$$

boils at 222—224°, has a sp. gr. 0·8814 at 0° and 0·8688 at 19°, and n_D 1·46875 at 19°, whence the molecular refraction is 61·4, whereas that calculated from the formula adopted is 63·64. This difference seems to imply the presence of a second closed chain, in which case the calculated molecular refraction would be 61·94. *Diethylcampholenyl acetate* is liquid, and decomposes even when heated under 14 mm. pressure. When campholenonitrile is treated with magnesium methyl iodide, a small yield (5 to 6 per cent.) of *methylcampholenone*,

$$\begin{matrix}CMe_2\cdot CMe\\ | \\ CH_2—CH_2\end{matrix}\!\!>\!C\cdot CH_2Ac,$$

is obtained; this boils at 210—212°, has a sp. gr. 0·9343 at 0° and 0·9247 at 15°, and n_D 1·47172 at 15°. *Ethylcampholenone*, similarly prepared, boils at 222—225°, has sp. gr. 0·9322 at 0° and 0·9210 at

16°, and n_D 1·46796 at 16°. When campholenolactone is treated with magnesium methyl iodide, *dimethylcampholandiol*,

$$\begin{array}{l}CMe_2\cdot CMe(OH)\\ \vert \\ CH_2 \text{———} CH_2\end{array}\!\!>CH\cdot CH_2\cdot CMe_2\cdot OH,$$

is formed; this melts at 92—94°, and is soluble in benzene and hot alcohol.

Oxydimethylcampholenol, $CH_2\!<\!\begin{array}{l}CMe_2\cdot CMe\text{—————}\\ \qquad\quad \vert \\ CH_2\text{—}C(CH_2\cdot CMe_2\cdot OH)\end{array}\!\!>O$, produced by the interaction of magnesium methyl iodide with ethyl ketocampholenate and decomposition of the magnesium compound first formed with water and sulphuric acid, crystallises from alcohol and melts at 142°. T. A. H.

Transformation Products of Pulegonehydroxylamine. CARL D. HARRIES and LOUIS ROY (*Ber.*, 1904, 37, 1341. Compare Abstr., 1898, i, 573, and Semmler, this vol., i, 437).—When pulegone is boiled with a solution of hydroxylamine hydrochloride in water, no pulegonehydroxylamine is produced, but an oily, basic compound. The same compound may be prepared by warming pulegonehydroxylamine with 20 per cent. hydrochloric acid on the water-bath, and is precipitated by potassium hydroxide as a yellow, viscous oil, which boils at 102—106° under 13 mm. pressure. It is derived from pulegonehydroxylamine by the loss of water, $C_{10}H_{19}O_2N - H_2O = C_{10}H_{17}ON$, and forms an oxalate and picrate. Its properties are under investigation. C. H. D.

Derivatives of Thujone. LEO TSCHUGAEFF (*Ber.*, 1904, 37, 1481—1486. Compare Semmler, this vol., i, 438; Kondakoff and Skworzoff, *ibid.*, 439).—The relationship of the formulæ proposed for α- and β-thujenes to those for α-tanacetonedicarboxylic acid and homotanacetonedicarboxylic acid, put forward by Semmler, is pointed out. *Thujamenthene*, $C_{10}H_{18}$, prepared by carefully decomposing the compound, $C_{10}H_{19}\cdot O\cdot CS\cdot SCH_3$, formed from thujamenthol, boils at 157—159° and has a sp. gr. 0·8046 at 20°/4° and n_D 1·44591 at 20°; it forms a crystalline nitrosochloride. E. F. A.

Essential Oils obtained by Extracting Fresh Flowers with Volatile Solvents (Essential Flower-extract Oils). HUGO VON SODEN (*J. pr. Chem.*, 1904, 69, 256—272).—These flower-extracts are obtained by extracting the fresh flowers in the cold with light petroleum and distilling off the solvent; they were freed from wax, colouring matters, &c., by solution in cold alcohol, and were finally distilled with steam, the distillate being extracted with ether.

Violets.—Yield of the purified oil: 0·003 per cent. of the fresh flowers; colour, pale greenish-yellow; sp. gr. 0·920 at 15°; rotation, +104°15′ (in 100 mm. tube?); acid number, 10; ester number, 37.

Orange flowers.—Yield: 0·06 per cent. Sp. gr. 0·9245 at 15°; rotation, −2°30′ in 100 mm. tube; acid number, 4; ester number, 102 (corresponding with 35·7 per cent. linalyl acetate); methyl anthranilate, 6 9 per cent. (leaving 26·7 per cent. linalyl acetate).

Reseda.—Yield : 0·003 per cent ; colour, yellow ; sp. gr. 0·961 at 15° ; rotation, +31°20′ at 17° in 100 mm. tube ; acid number, 16 ; ester number, 85 ; solidifies when cooled.

Roses.—*French* : Yield : 0·52 per cent. ; colour, reddish-yellow ; sp. gr. 0·967 at 15° ; rotation, −1·55° at 17° in 100 mm. tube ; acid number, 5·5 ; ester number, 4·6 (corresponding with 1·6 per cent. of geranyl acetate) ; acetyl number, 295 ; solidifies at 7—5°. Contains phenylethyl alcohols, 60 ; aliphatic terpene alcohols (geraniol, nerol, citronellol), 20 per cent. *German* : Yield : 1·07 per cent. ; colour, golden-yellow ; sp. gr. 0·984 at 19° ; rotation, +0°9′ at 17° ; acid number, 3 ; ester number, 4 (corresponding with 1·40 per cent. of geranyl acetate) ; acetyl number, 313·5 ; solidifies at 18—12°. Contains phenylethyl alcohol, 75 ; primary aliphatic terpene alcohols, 15 per cent.

Jasmine (2 samples).—Yield : 0·077, 0·072 per cent. ; colour, reddish-yellow ; sp. gr. 0·9955, 0·967, at 15° ; rotation, −1°, feebly, in 100 mm. tube ; acid number, 2·5, 3·5 ; ester number, 190, 161·5 (corresponding with 51, 43·3, per cent. of benzyl acetate). Contains indole.

Cassia.—Yield : 0·084 per cent. ; colour, reddish-yellow ; sp. gr. 1·047 at 27° ; rotation, −0°40′ at 25° in 100 mm. tube ; acid number, 42·5 (corresponding with 10·3 per cent. of salicylic acid) ; ester number, 114 (corresponding with 30·9 per cent. of methyl salicylate) ; solidifies at 21—18°. C. F. B.

Oil of Jasmine Blossoms. VII. ALBERT HESSE (*Ber.*, 1904, 37, 1457—1463. See Abstr., 1901, i, 732).—In two experiments, the extract, obtained by treatment of fresh jasmine blossoms, gave no reaction for methyl anthranilate until after distillation in steam, when the ethereal oil (yield, 0·0447 and 0·0442 per cent.) was found to contain 0·42—0·377 per cent. of methyl anthranilate and 2·1—2·0 per cent. of indole.

An ethereal extract of fresh blossoms gave no reaction for methyl anthranilate either before or after distillation in steam. The ethereal oil gave no reaction for indole. The author considers that the anthranilate and the indole are present in the fresh blossoms as compounds which are easily decomposed by distillation, by the process of "enfleurage," and even by extraction under certain conditions.

G. Y.

Two New Algerian Essential Oils. PAUL JEANCARD and C. SATIE (*Bull. Soc. chim.*, 1904, 31, 478—480).—Scheih oil is reddish-brown, with an odour resembling that of absinthe, and is soluble in its own volume of alcohol (80°). It has a sp. gr. 0·9540 at 9·5°, specific viscosity 170 seconds at 9·5°, acid number 8·4, and saponification values 66·5 and 129·5 respectively before and after acetylation. It contains 15 per cent. of phenolic substances, of which pyrogallol dimethyl ether was isolated. The oil, after removal of phenols, gave on fractional distillation 15 per cent. below 190°, 17·4 per cent. between 190° and 200°, and 48 per cent. above 200°. The two latter fractions probably contain respectively thujone and thujol.

Gouft oil is bright yellow and possesses a terpenoid odour; it has a sp. gr. 0·8720 at 9·5°, acidity 1·12, and saponification values 14 and 42 respectively before and after acetylation: 4·6 per cent. of the oil distils below 155°, the same proportion between 155° and 160°, 44·4 per cent. from 160° to 165° and 13 per cent. from 165° to 170°. The third fraction contains *l*-pinene and the last a primary alcohol with a geraniol-like odour. T. A. H.

Synthesis of Quercitol. Stanislaus von Kostanecki, Victor Lampe, and Josef Tambor (*Ber.*, 1904, **37**, 1402—1405).—Kostanecki and Tambor's 2′-hydroxy-4′ : 6′ : 3 : 4-tetramethoxychalkone (this vol., i, 426), when boiled with dilute hydrochloric acid and alcohol, yields 5 : 7 : 3′ : 4′-*tetramethoxyflavanone*,

$$C_6H_2(OMe)_2<\begin{matrix}O-CH\cdot C_6H_3(OMe)_2\\ CO\cdot CH_2\end{matrix},$$

which crystallises from carbon disulphide in colourless, thick needles, melting at 159—160°, and soluble in sodium hydroxide solution. Amyl nitrite and concentrated hydrochloric acid convert this into an *iso-nitroso*-derivative, $C_6H_2(OMe)_2<\begin{matrix}O-CH\cdot C_6H_3(OMe)_2\\ CO\cdot C:N\cdot OH\end{matrix}$, which crystallises from benzene in small, almost colourless needles melting and decomposing at 183°, and soluble in alkali and in concentrated sulphuric acid. When dissolved in acetic acid and boiled with 10 per cent. sulphuric acid, the *iso*nitroso compound yields hydroxylamine and 5 : 7 : 3′ : 4′-*tetramethoxyflavonol*, which crystallises in yellow needles melting at 197—198°. This does not dissolve in cold alkalis, and, with warm sodium hydroxide, it yields a sparingly soluble, yellow *sodium* derivative. It dyes alumina and iron mordants to a certain extent, and, when boiled for some time with concentrated hydriodic acid, yields quercitol (5 : 7 : 3′ : 4′-tetrahydroxyflavonol),

$$C_6H_2(OH)_2<\begin{matrix}O-C\cdot C_6H_3(OH)_2\\ CO\cdot C\cdot OH\end{matrix}.$$

When purified by aid of its acetyl derivative and crystallised from dilute alcohol, it forms lemon-yellow, glistening needles melting and decomposing at 313—314°. Its *penta-acetyl* derivative melts at 193—194°. J. J. S.

Reactivity of Substituted Phloroglucinols in the Formation of Fluorones. A. Schreier and Franz Wenzel (*Monatsh.*, 1904, **25**, 311—318. Compare Abstr., 1900, i, 308).—When warmed together with hydrochloric acid, methylphloroglucinolcarboxylic acid and salicylaldehyde react easily with evolution of carbon dioxide. On cooling, the reaction mixture solidifies to a mass of delicate, red needles, which consist of a mixture of the hydrochlorides of 8-hydroxy-5-(or 7-)-methylfluorone and of 8-hydroxy-5-(or 7-)-methylfluoronecarboxylic acid. On boiling with concentrated hydrochloric acid, the carboxylic group is completely eliminated, and, on cooling, the hydrochloride of 8-hydroxymethylfluorone, $C_{14}H_{10}O_3$,HCl, separates in violet, metallic crystals.

The action of bromine in chloroform solution on methylphloro-

glucinolcarboxylic acid leads to the formation of dibromomethylphloroglucinol, which melts at 132—134° and is insoluble in aqueous potassium hydrogen carbonate, and *bromomethylphloroglucinolcarboxylic acid*, $C_8H_7O_5Br,H_2O$, which crystallises in delicate, white needles, melts at 149° or at 159—161° when anhydrous, and gives a blue coloration with ferric chloride. When boiled with water, it loses carbon dioxide and yields *bromomethylphloroglucinol*, $C_7H_7O_3Br,4H_2O$, which crystallises in long, transparent, yellow needles, melts at 129—130°, and loses $4H_2O$ when heated at 100°.

Bromomethylphloroglucinol and salicylaldehyde, when heated in acetic acid solution along with hydrochloric acid, enter into reaction, but, on cooling, there is no crystalline separation. On the addition of water, a red, amorphous *substance* is precipitated. This is soluble in alcohol, benzene, or chloroform, but cannot be obtained in the crystalline state.

The introduction of a bromine atom into methylphloroglucinol does not favour the fluorone formation, as does the presence of a carboxylic group. G. Y.

8-Hydroxy-5 : 7-dimethylfluorone. J. LIEBSCHÜTZ and FRANZ WENZEL (*Monatsh.*, 1904, **25**, 319—331. See foregoing abstract).—Dimethylphloroglucinol methyl ether $[Me_2 : OMe : (OH)_2 = 1 : 3 : 4 : 2 : 6]$ (Bosse, Abstr., 1901, i, 207) and salicylaldehyde in acetic acid solution give an intense red coloration immediately on addition of concentrated hydrochloric acid. The product, 8-*methoxy*-5 : 7-*dimethylfluorone* (?), is precipitated as a red, amorphous mass on addition of water. It is soluble in methyl or ethyl alcohol, ether, or benzene, and is precipitated from its solution in aqueous sodium hydroxide on addition of sulphuric acid. When warmed with concentrated hydrochloric acid, it yields 8-hydroxy-5 : 7-dimethylfluorone, from which it can be formed by the action of diazomethane.

Under the same conditions, dimethylphloroglucinol methyl ether $[Me_2 : OMe : (OH)_2 = 1 : 3 : 2 : 4 : 6]$ (Abstr., 1902, i, 464) condenses with salicylaldehyde only on prolonged contact. The bluish-grey, amorphous *product*, which is precipitated on addition of water, does not yield hydroxydimethylfluorone. These facts confirm the constitution assigned to 8-hydroxy-5 : 7-dimethylfluorone.

Reduction of 8-hydroxy-5 : 7-dimethylfluorone with sodium amalgam leads to the formation of a *leuco*-compound,

$$\begin{matrix} CMe\cdot C(OH){:}C\cdot CH_2 \\ C(OH)\cdot CMe{:}C\text{--}CO \end{matrix} > C_6H_4,$$

which crystallises in colourless needles, melts at 185—186°, is oxidised easily on exposure to air, and forms a *diacetyl* derivative. This crystallises in yellow needles and melts at 117—118°.

The action of 1 mol. bromine on 8-hydroxy-5 : 7-dimethylfluorone leads to the formation of a *monobromo*-substitution product,

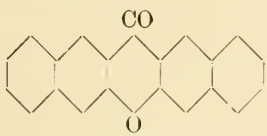
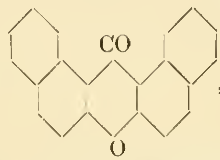
$$\begin{matrix} CBrMe\cdot CO\cdot C{:}CH \\ CO\text{——}CMe{:}C\cdot CO \end{matrix} > C_6H_4,$$

which crystallises in ruby-coloured prisms and decomposes at 170—180°.

With bromine, the monobromo-compound forms an *additive* compound, $\begin{matrix} CBrMe\cdot CO\cdot CBr\cdot CHBr \\ CO—CMe\!:\!C——CO \end{matrix}\!\!>C_6H_4$ (?), which is obtained as an amorphous mass. With methyl alcohol, it evolves hydrogen bromide and yields a *dibromomethoxy*-derivative, $\begin{matrix} CBrMe\cdot CO\cdot CBr\cdot CH(OMe) \\ CO—CMe\!:\!C———CO \end{matrix}\!\!>C_6H_4$, which crystallises in yellow, transparent plates, melts at 117—118°, and becomes red when exposed to light. The *dibromoethoxy*-derivative, formed by the action of ethyl alcohol on the tribromo-compound, crystallises in yellow, hexagonal plates and melts at 102—104°.

G. Y.

The Dinaphthaxanthene Series. ROBERT FOSSE (*Compt. rend.*, 1904, **138**, 1051—1054. Compare Abstr., 1901, i, 604, 643; 1902, i, 171, 304, 368, 689; 1903, i, 49, 357; this vol., i, 82, 336, 337).—Of the dinaphthaxanthones,

γ,  and α, ,

the first (γ) was prepared by Kostanecki from ββ'-naphtholcarboxylic acid and melts at 241° (Abstr., 1892, 1099), whilst the second (α) was prepared by Bender from β-naphthyl ethyl carbonate (Abstr., 1881, 48) and by Kostanecki from αβ-hydroxynaphthoic acid, and can also be obtained by the action of an alkali carbonate on β-naphthyl carbonate according to the equation: $2CO(OC_{10}H_7)_2 = CO_2 + 2C_{10}H_7OH + CO{<}{\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}}{>}O$; it melts at 194° and, on reduction with nascent hydrogen, yields dinaphthaxanthhydrol,

$$HO\cdot CH{<}{\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}}{>}O,$$

m. p. 145°, from which dinaphthaxanthonium salts, $CH{<}{\begin{matrix}C_{10}H_6\\ \text{———} \\C_{10}H_6\end{matrix}}{>}OX$, are obtained by the action of hydracids, and dinaphthaxanthene, $CH_2{<}{\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}}{>}O$, melting at 201°, by the action of acetic acid and alcohol.

A compound obtained by Bender by oxidising methyldinaphthaxanthene, $CHMe{<}{\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}}{>}O$, melting at 149°, described as a third dinaphthaxanthone, has probably a different constitution, since it gives a reduction product melting at 165°.

M. A. W.

The Indophenine Reaction. FRANZ W. BAUER (*Ber.*, 1904, **37**, 1244—1245. Compare Schwalbe, this vol., i, 337).—Thiophen, in benzene solution, fails to give the indophenine reaction with isatin when pure sulphuric acid is employed; if, however, a trace of ferric

chloride or nitric acid is added to the acid, the characteristic deep blue colour is at once produced. W. A. D.

Bromine Derivatives of the Cinchona Alkaloids, and the Corresponding Compounds containing less Hydrogen. A. Christensen (*J. pr. Chem.*, 1904, [ii], 69, 193—222. Compare Abstr., 1901, i, 481; 1904, i, 184).—Skalweit's dibromocinchonidine and dihydroxycinchonidine (Abstr., 1874, 808) must have been cinchonidine dibromide and dehydrocinchonidine respectively. Galimard's α- and β-dibromocinchonidines (Abstr., 1901, i, 162) were probably both cinchonidine dibromide.

Bromocinchonidine, $C_{19}H_{21}ON_2Br$, obtained by the action of cold alcoholic potassium hydroxide on cinchonidine dibromide, melts at 218° and has $[\alpha]_D$ $-110\cdot3°$ in 2 per cent. solution in a mixture of chloroform and alcohol (2 : 1 vols.); its *oxalate*, $2C_{19}H_{21}ON_2Br,C_2H_2O_4,2H_2O$, and a *hydrobromide*, $C_{19}H_{21}ON_2Br,2HBr,2H_2O$, were analysed. Prolonged boiling with alcoholic potassium hydroxide converts it into *dehydrocinchonidine*, $C_{19}H_{20}ON_2$, which melts at 194°; the *oxalate*,

$$2C_{19}H_{20}ON_2,C_2H_2O_4,H_2O,$$

melting just above 190°, and *hydrochloride*, $C_{19}H_{20}ON_2,HCl,2H_2O$, of this base were analysed. The base, when treated with hydrogen bromide and bromine in acetic acid solution, forms *dibromocinchonidine hydrobromide perbromide*, $C_{19}H_{20}ON_2Br_2,2HBr,Br_2$; by treating this with sulphurous acid and precipitating with ammonia, *dibromocinchonidine*, $C_{19}H_{20}ON_2Br_2$, melting at 186°, is obtained.

Bromoquinine, $C_{20}H_{23}O_2N_2Br$, obtained from quinine dibromide, melts at 210° and has $[\alpha]_D$ $-118\cdot1°$; the *hydrochloride*,

$$C_{20}H_{23}O_2N_2Br,2HCl,H_2O,$$

hydrobromide, $C_{20}H_{23}O_2N_2Br,2HBr,3H_2O$ and anhydrous, *sulphate*, $2C_{20}H_{23}O_2N_2Br,H_2SO_4,7H_2O$, and *herepathite*,

$$4C_{20}H_{23}O_2N_2Br,3H_2SO_4,2HI,I_4,$$

were analysed. *Dehydroquinine*, $C_{20}H_{22}O_2N_2$, was obtained in the crystalline state, although not without difficulty; it melts at 184°, has $[\alpha]_D$ $-178°$ and $-180°$ respectively in 1·42 and 2·85 per cent. solution in a mixture of chloroform and alcohol, and dissolves in water to the extent of 0·246 gram in 100 c.c. The *oxalate*, $2C_{20}H_{22}O_2N_2,C_2H_2O_4,xH_2O$, melting at 133—134°, *hydrochloride*, $C_{20}H_{22}O_2N_2,HCl,xH_2O$, and *herepathite*, $4C_{20}H_{22}O_2N_2,3H_2SO_4,2HI,I_4$, were analysed; the last was amorphous and not quite pure. Dehydroquinine appears to form a dibromo-additive product, presumably dibromoquinine, but this could not be obtained pure. C. F. B.

Synthesis of Nicotine. Amé Pictet and Arnold Rotschy (*Ber.*, 1904, 37, 1225—1235).—The following results were necessary to render the synthesis of nicotine from 3-aminopyridine complete (compare Pictet and Crépieux, Abstr., 1895, i, 627; 1898, i, 688; Pictet, Abstr., 1900, i, 685). (1) The production of nicotyrine from its methiodide; (2) the identification of tetrahydronicotyrine with *i*-nicotine; (3) the resolution of *i*-nicotine into its optical antipodes and the identification of the *l*-form with the natural alkaloid. These have been successfully realised.

Attempts to remove methyl iodide from nicotyrine methiodide by

dry distillation were without issue, and on heating the methiodide with water for 3 hours at 200° a base was obtained which yielded a picrate melting at 120°, and was therefore obviously not identical with nicotyrine. The desired result was, however, obtained by distilling the methiodide with lime; it was identified by its boiling point, by its picrate, melting at 162°, and by its platinichloride.

Tetrahydronicotyrine was identified as *i*-nicotine (*loc. cit.*) by its boiling point, density, and by its giving the same platinichloride, $C_{10}H_{14}N_2,H_2PtCl_6,H_2O$; the *picrate* melts at 218°, the *dihydriodide* at 195°, and the *dimethiodide* at 219°. The resolution of the acid into its components was effected by means of the ditartrate, $C_{10}H_{14}N_2,2C_4H_6O_6,2H_2O$, which is best prepared in aqueous, not alcoholic, solution (compare Dreser, Abstr., 1889, 730). *l*-Nicotine *d*-ditartrate has $[\alpha]_D$ +27·16° at 15° and +26·60° at 27°, calculated for the anhydrous salt; it melts at 88—89° and is much less soluble than *d*-nicotine *d*-ditartrate, which can only be obtained as a syrup. *l*-Nicotine, prepared from the ditartrate, boils at 246—246·5° under 734·5 mm. pressure, has a sp. gr. 1·0177 at 10°/4°, 1·0092 at 20°/4°, and $[\alpha]_D$ −160·93° at 20°; the corresponding values obtained with natural nicotine are respectively 246·1—246·2° under 730·5 mm. pressure, sp. gr. 1·0180 and 1·0097, and $[\alpha]_D$ −166·39° at 20°.

d-*Nicotine* was obtained by liberating the base from its syrupy *d*-ditartrate, and converting it by means of *l*-tartaric acid into d-*nicotine* l-*ditartrate*, which crystallises from water, melts at 88—89°, and has $[\alpha]_D$ − 25·58° at 15°; d-*nicotine* boils at 245·5—246·5° under 729 mm. pressure, has a sp. gr. 1·0171 at 10°/4°, 1·0094 at 20°/4°, and $[\alpha]_D$ + 163·17° at 20°.

Experiments made by Prof. A. Mayor to ascertain the relative poisoning effects of *d*- and *l*-nicotines are appended; it appears that *l*-nicotine is twice as poisonous as the *d*-base, and produces totally different symptoms. W. A. D.

Composition of Yohimbine and its Relationship to Yohimboaic Acid. LEOPOLD SPIEGEL [and ERNST B. AUERBACH] (*Ber.*, 1904, **37**, 1759—1766. Compare Abstr., 1899, i, 966; 1903, i, 274).—Crystallised yohimbine as obtained from plants loses a molecule of water forming *anhydroyohimbine*, $C_{22}H_{28}O_3N_2$; the salts of yohimbine are derived from the latter compound; thus the *nitrate*, $C_{22}H_{28}O_3N_2,HNO_3$, crystallises in large, colourless prisms melting at 276°. The following esters of yohimboaic acid (noryohimbine) have been prepared: the *ethyl* ester crystallises in glistening needles melting at 189°, the *propyl* ester melts at 135—136°, and the iso*butyl* ester crystallises in platelets melting at 137—138°. These compounds contain two alkyl groups, one being attached to nitrogen; yohimboaic acid is monobasic. E. F. A.

A New General Reaction of Aldehydes. LOUIS J. SIMON and A. CONDUCHÉ (*Compt. rend.*, 1904, **138**, 977—980).—Ethyl oxalacetate condenses readily with aldehydes in the presence of ammonia to form the ammonium salts of substituted derivatives of diketodihydropyrrolinecarboxylic acids, from which the free acid is liberated by hydrochloric acid. *Ethyl 2-phenyldiketodihydro-*

pyrroline-3-carboxylate, $NH<\begin{matrix}CO—CO\\ CHPh\cdot CH\cdot CO_2Et\end{matrix}$, the compound formed by benzaldehyde, is a white, crystalline solid decomposing without melting at 185°, is slightly soluble in cold alcohol and less so in water, dissolves in cold concentrated acids, and is reprecipitated by water; gives a blue coloration when heated with fuming sulphuric acid; is neutral to litmus and acid to phenolphthalein, is soluble in dilute alkalis and in boiling alkali carbonates, and reprecipitated by dilute acids. The *potassium* and *silver* derivatives are described. The *copper* derivative, $(C_{13}H_{12}O_4N)_2Cu,2C_2H_4O_2$, crystallises in characteristic green crystals containing 2 mols. of acetic acid, which it loses at 150°, is insoluble in water, but soluble in ammonia or concentrated nitric or acetic acid, and does not decompose at 200°. Both the acids and its salts develop a red coloration with ferric chloride, and the ketonic nature of the compound is displayed in the formation of a *phenylhydrazone* melting at 172—173°, and an *oxime* very soluble in alcohol and crystallising with water of crystallisation, the hydrated compound melting at 100°, the anhydrous at 150°.

The decomposition temperatures of similar compounds obtained with other aldehydes are as follows: with *m*-nitrobenzaldehyde, 173°; with salicylaldehyde, 175°; with anisaldehyde, 160°; with vanillin, 180°; and with piperonal, 155°.

The ammonia in this reaction can be replaced by a primary, but not by a secondary amine, the compound obtained by the interaction of ethyl oxalacetate, benzaldehyde, and aniline having the composition $NPh<\begin{matrix}CO—CO\\ CHPh\cdot CH\cdot CO_2Et\end{matrix}$. [This compound has already been described by Schiff and Bertini. Compare Abstr., 1897, i, 293.]

M. A. W.

Compounds of Pyridine with Nitrates of Bivalent Metals. HERMANN GROSSMANN (*Ber.*, 1904, 37, 1253—1257).—*Copper nitrate pyridine*, $Cu(NO_3)_2,4C_5H_5N$, formed on adding a saturated solution of copper nitrate to an excess of pyridine, crystallises in strongly pleochroic pyramids and loses its pyridine on exposure to air.

The double salts, $Ca(NO_3)_2,2C_5H_5N,2H_2O$; $Zn(NO_3)_2,2C_5H_5N,2H_2O$; $Mn(NO_3)_2,2C_5H_5N,2H_2O$, were obtained by adding pyridine to the aqueous solutions of the metallic nitrates and concentrating the solutions obtained over sulphuric acid. They have, in the sense of Werner's hypothesis, the general formula, $[Me(2Py)(2H_2O)](NO_3)_2$.

On dissolving cobalt bromide in pyridine, rose-coloured, microscopic, rhombic plates of the *salt* $CoBr_2,4C_5H_5N$ separate; on dissolving it in hydrobromic acid and concentrating the solution, large, bluish-green, hygroscopic plates of *pyridinium cobalt bromide*,

$$(C_5H_5N)_2CoBr_4,2H_2O,$$

are obtained. The hexapyridine compound, $CoBr_2,6C_5H_5N$, could not be isolated.

W. A. D.

Constitution of Platinum Bases. PETER KLASON (*Ber.*, 1904, 37, 1349—1360. Compare Abstr., 1903, i, 224).—*a-Platopyridine-ammine chloride*, $C_5H_5N\dot{:}PtCl\cdot NH_3Cl$, prepared from pyridine and

potassium platosemiammine chloride, or from ammonia and potassium platosemipyridine chloride, crystallises in yellow prisms and dissolves in 240 parts of water at the ordinary temperature.

Platosemipyridine-ethylsulphine chloride, $C_5H_5N{:}PtCl{\cdot}SEt_2Cl$, prepared from platosemiethylsulphine chloride and pyridine, melts at 96°, but when maintained in the fused state for a short time passes into the isomeric *platosemiethylsulphinepyridine chloride*,

$$SEt_2{:}PtCl{\cdot}C_5H_5NCl,$$

melting at 160°. The latter compound is also obtained from potassium platosemipyridine chloride and ethyl sulphide. Silver nitrate converts it into a third isomeride, *platosemipyridinesemiethylsulphine chloride*, $SEt_2Cl{\cdot}Pt{\cdot}C_5H_5NCl$, crystallising from alcohol or chloroform in colourless needles, and melting and decomposing at 165°. A mixture of the first two isomerides is obtained by the action of pyridine on α- or β-platoethylsulphine chloride.

Platosemiethylsulphinesemidiammine chloride,

$$NH_3{:}Pt(NH_3Cl){\cdot}SEt_2Cl,$$

prepared from α-platosemidiammine chloride and ethyl sulphide, could not be obtained in a crystalline form. Its solution passes partially into the isomeric platosemiamminesemiethylsulphineammine chloride, $SEt_2{:}Pt(NH_3Cl)_2$.

β-Platosemidiammine chloride and ethyl sulphide form the unstable platosemiamminesemiethylsulphineammine chloride.

Platosemidiamminesemidipyridine chloride,

$$\begin{matrix}NH_3 \\ C_5H_5N\end{matrix}{\gg}Pt{<}\begin{matrix}NH_3Cl \\ C_5H_5NCl\end{matrix}, H_2O,$$

obtained in solution by Jörgensen (Abstr., 1886, 857), crystallises in cauliflower-like, readily soluble masses.

The paper also contains a theoretical discussion of the isomerism and tautomerism of the platinum bases. C. H. D.

2 : 6-Lutidine-3 : 5-dicarboxylic Acid. Ernst Mohr and W. Schneider (*J. pr. Chem*, 1904, **69**, 245—255).—2 : 6-Dimethylpyridine-3 : 5-dicarboxylic acid (Engelmann, Abstr., 1886, 259) was obtained by preparing ethylic dihydrolutidinecarboxylate (Knoevenagel and Klages, Abstr., 1895, i, 51), oxidising it in suspension in alcohol at 40° with nitrous anhydride (or, on a smaller scale, by warming it with 1·1 mols. of 20—25 per cent. nitric acid), and hydrolysing the resulting ester with 1·35 times the calculated amount of alcoholic potassium hydroxide. The acid was purified by crystallisation from water and by passage through the silver salt; it then gave satisfactory numbers on analysis, corresponding with an anhydrous acid (not one with $\frac{1}{2}H_2O$). The pure acid melts at 315° to 320° according to the rapidity of heating; 1 part dissolves in 97—98 parts of boiling, and in about 3250 of cold water; in 150—160 of boiling and in about 290 of cold alcohol.

C. F. B.

α- and γ-Phenylpyridylcarbinols. Alexei E. Tschitschibabin (*Ber.*, 1904, **37**, 1370—1372).—Zinc dust and sodium ethoxide reduce α- and γ-phenyl pyridyl ketones (2- and 4-benzoylpyridines) (Abstr., 1902, i, 175) to the corresponding carbinols.

Phenyl-2-pyridylcarbinol, $C_5NH_4 \cdot CHPh \cdot OH$, separates from benzene on addition of light petroleum in large, transparent crystals, melts at 82°, and dissolves very readily in alcohol, ether, or benzene. Dilute acids dissolve it, and it is reprecipitated on addition of alkali. The sparingly soluble *platinichloride* crystallises in orange-red leaflets and melts and decomposes at 197°.

Phenyl-4-pyridylcarbinol separates from benzene or ethyl acetate in small, white crystals, melts at 126°, and dissolves readily in alcohol, sparingly in ether or benzene. The sparingly soluble *platinichloride* crystallises in orange scales and melts at 205°.

Alkaline potassium permanganate oxidises both carbinols to the original ketones. C. H. D.

Oxidation of Benzylated and Phenylated Pyridines. Alexei E. Tschitschibabin (*Ber.*, 1904, 37, 1373—1374).—When benzylpyridines (Abstr., 1903, i, 853) are oxidised by potassium permanganate in acid solution, the benzene ring is destroyed and pyridinecarboxylic acids are formed; in neutral solution, however, the pyridine ring is attacked, with the formation of benzoic acid (Abstr., 1901, i, 484). Similar results were obtained by Skraup and Cobenzl in the oxidation of 3-phenylpyridine (Abstr., 1883, 1010).

When a mixture of 2- and 4-phenylpyridines prepared by the action of solid sodium nitrite and acetic acid on a mixture of aniline and pyridine (compare Möhlau and Berger, Abstr., 1893, i, 701) is oxidised with potassium permanganate in neutral or alkaline solution, benzoic acid is obtained. In acid solution, *iso*nicotinic and picolinic acids are obtained. These results are in accordance with Vorländer's rule (Abstr., 1901, i, 454) that compounds with tervalent nitrogen pass into saturated compounds with quinquevalent nitrogen in acid solution. C. H. D.

Condensation of 2- and 4-Benzylpyridines with Formaldehyde. Alexei E. Tschitschibabin (*J. pr. Chem.*, 1904, [ii], 69, 310—320. Compare Stoehr, Abstr., 1892, 628; Koenigs and Happe, Abstr., 1903, i, 850).—When heated with 40 per cent. formaldehyde at 150°, but not at 100°, 2-benzylpyridine is converted into phenyl-2-pyridyldimethylolmethane and α-phenyl-α-2-pyridylethylene.

Phenyl-2-pyridyldimethylolmethane, $C_5NH_4 \cdot CPh(CH_2 \cdot OH)_2$, crystallises in needles and melts at 106—107°. The *platinichloride*,

$$(C_{14}H_{15}O_2N)_2,H_2PtCl_6,$$

crystallises in needles; the *picrate* is a yellow, crystalline powder and melts at 180°.

α-Phenyl-α-2-pyridylethylene, $C_5NH_4 \cdot CPh{:}CH_2$, is a viscid oil, which distils at 292—295° with slight decomposition, is soluble in dilute mineral acids, and forms an additive compound with bromine. The *picrate*, $C_{13}H_{11}N,C_6H_3O_7N_3$, crystallises in long, glistening, yellow prisms and melts at 155°; the *platinichloride* forms large, red leaflets and melts at 175°; the mother liquor from the picrate contains a small quantity of a *substance*, probably methylolphenylpyridylmethane.

2-Benzylpyridine and formaldehyde yielded a slight amount of α-phenyl-α-2-pyridylethylene when exposed to direct sunlight for

3 weeks. When heated with 40 per cent. formaldehyde at 100°, 4-benzylpyridine forms phenyl-4-pyridyldimethylolmethane, phenyl-4-pyridylmethylolmethane, and α-phenyl-α-4-pyridylethylene; at 50°, phenyl-4-pyridyldimethylolmethane only is formed; on exposure to direct sunshine for 15 days, the glycol and a trace of the ethylene compound are obtained.

Phenyl-4-pyridyldimethylolmethane, $C_5NH_4\cdot CPh(CH_2\cdot OH)_2$, crystallises in delicate needles and melts at 194°. The *platinichloride*, $(C_{14}H_{15}O_2N)_2,H_2PtCl_6$, forms small, glistening, orange-red crystals and melts at 185°.

Phenyl-4-pyridylmethylolmethane, $C_5NH_4\cdot CHPh\cdot CH_2\cdot OH$, crystallises in prisms or leaflets and melts at 89—90°. The *platinichloride*, $(C_{13}H_{13}ON)_2,H_2PtCl_6$, forms red crystals and melts at 160°. 4-Benzoylpyridine is formed by oxidation of phenyl-4-pyridylmethylolmethane with potassium permanganate.

α-Phenyl α-4-pyridylethylene, $C_{13}H_{11}N$, is an oil which boils at 300—305° and forms an additive *compound* with bromine. The platinichloride, $(C_{13}H_{11}N)_2,H_2PtCl_6$, crystallises in delicate, yellow needles and melts at 182—185°. G. Y.

Condensation Products of the Three Nitrobenzaldehydes [with Ethyl Cyanoacetate in presence of Ammonia]. Giovanni Issoglio (*Atti R. Accad. Sci. Torino*, 1904, 39, 140—160. Compare Guareschi, Abstr., 1898, i, 274, and 1902, i, 52).—The *ammonium* derivative of 3 : 5-*dicyano*-6-*hydroxy*-4-m-*nitrophenyl*-$\Delta^{3\cdot 6}$-*dihydropyridone*, $N{<}{\begin{matrix}C(ONH_4)\cdot CH(CN)\\ CO\text{——————}C(CN)\end{matrix}}{>}C\cdot C_6H_4\cdot NO_2$, is the principal product when *m*-nitrobenzaldehyde is condensed with ethyl cyanoacetate and ammonia at the ordinary temperature; it crystallises from hot water in slightly yellow prisms, does not melt at 300°, and when warmed with dilute sulphuric acid gives β-m-*nitrophenylcyanovinylacetic acid*, $NO_2\cdot C_6H_4\cdot C(:CH\cdot CN)\cdot CH_2\cdot CO_2H$. On decomposing the barium or silver salt corresponding with the foregoing ammonium derivative with cold dilute sulphuric acid or hydrogen sulphide respectively, 3 : 5-*dicyano*-6-*hydroxy*-4-m-*nitrophenyl*-$\Delta^{3\cdot 6}$-*dihydropyridone* is obtained; it is very soluble in water, alcohol, acetic acid, and ethyl acetate, melts and decomposes at 260°, and gives a *silver* derivative, $C_{13}H_5O_4N_4Ag,4H_2O$, a *barium* derivative, $(C_{13}H_5O_4N_4)_2Ba,7H_2O$, and a bluish-green *cuprammonium* compound, $C_{13}H_5O_4N_4Cu,2NH_3,3H_2O$; the latter, when heated at 90—100°, gives a grass-green salt,

$$C_{13}H_5O_4N_4Cu,1\tfrac{1}{2}NH_3,1\tfrac{1}{2}H_2O.$$

Together with the foregoing pyridone, m-*nitrobenzylcyanoacetamide*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2$, is formed; it crystallises from water or alcohol in white, silky needles, melts at 147—148°, and on hydrolysis with aqueous barium hydroxide gives *m*-nitrobenzylmalonic acid. A *compound*,

$$NO_2\cdot C_6H_4\cdot CH:C(CN)\cdot CO\cdot NH_2,NO_2\cdot C_6H_4\cdot CH:C(CN)\cdot CO_2Et,$$

similar to Carrick's salt (Abstr., 1892, 1086), was also isolated from the condensation; it crystallises from alcohol and melts at 186·5°.

3 : 5-*Dicyano*-6-*hydroxy*-4-p-*nitrophenyl*-$\Delta^{3\cdot 6}$-*dihydropyridone*, prepared in the same way as the analogous *m*-nitro-compound, crystallises from alcohol in prismatic needles, melts and decomposes at 270—275°,

and gives a crystalline *barium* derivative, $(C_{13}H_5O_4N_4)_2Ba,6H_2O$, and an *ammonium* derivative with $1\frac{1}{2}H_2O$. p-*Nitrobenzylcyanoacetamide* crystallises from dilute alcohol in colourless needles melting at 168.5°. The *p*-nitro-compound, $C_{22}H_{17}O_7N_5$, corresponding with Carrick's compound, separates from alcohol of 90° in small, white, silky prisms and melts at 194—195°.

On condensing *o*-nitrobenzaldehyde with ammoniacal ethyl cyanoacetate, an entirely different reaction ensues from that occurring in the case of the meta- and para-compounds. A large proportion of resin is formed and small quantities of *o*-azoxybenzoic acid (?) and trinitrohydrobenzamide, $NO_2{\cdot}C_6H_4{\cdot}CH(N{:}CH{\cdot}C_6H_4{\cdot}NO_2)_2$, are produced. With cyanoacetamide, *o*-nitrobenzaldehyde in presence of dilute ammonia gives only o-*nitrobenzylidenecyanoacetamide*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}C(CN){\cdot}CO{\cdot}NH_2,$$

which crystallises from dilute alcohol in long, silky needles and melts at 173—174°. W. A. D.

Nitroindoles. FRANCESCO ANGELICO and G. VELARDI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 241—244).—3-*Nitroindole*,

$$C_6H_4{<}\begin{matrix}C(NO_2)\\NH\end{matrix}{>}CH \text{ or } C_6H_4{<}\begin{matrix}C({:}NO{\cdot}OH)\\N\end{matrix}{>}CH,$$

which cannot be obtained from indole by nitration with nitric acid, is easily prepared by the action of ethyl nitrate and sodium ethoxide on indole dissolved in absolute ether; it crystallises from benzene in yellow needles and melts at 210°. 3-Nitro-2-methylindole, obtained similarly from 2-methylindole, is identical with the compound formed by the oxidation of 3-nitroso-2-methylindole (Abstr., 1901, i, 45), and, on further nitration with nitric acid, gives Zatti's dinitromethylindole (Abstr., 1890, 897); on oxidation with potassium permanganate, 3-*nitroindole-2-carboxylic acid*, $C_6H_4{<}\begin{matrix}C(NO_2)\\NH\end{matrix}{>}C{\cdot}CO_2H$, is obtained, which crystallises from xylene in intensely yellow spangles and melts and decomposes at 230°, giving a sublimate consisting of 3-nitroindole. W. A. D.

Nitrosoindoles. ANGELO ANGELI and FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 255—258. Compare Angeli and Spica, Abstr., 1899, i, 938; Angelico and Calvello, 1901, i, 747; 1904, i, 188).—When 1-hydroxy-2-phenylindole, $C_6H_4{<}\begin{matrix}CH\\N(OH)\end{matrix}{>}CPh$ (Fischer and Hütz, Abstr., 1895, i, 371), is caused to interact with amyl nitrite in alcoholic solution containing sodium ethoxide, a *substance* $C_{14}H_{10}O_2N_2$, probably having the constitution

$$C_6H_4{<}\begin{matrix}C(NO)\\N(OH)\end{matrix}{>}CPh \text{ or } C_6H_4{<}\begin{matrix}C({:}N{\cdot}OH)\\NO\end{matrix}{>}CPh,$$

is obtained; it melts at 240°, gives an acetyl, benzoyl, and ethyl derivative, and on reduction with zinc and acetic acid is converted into 3-amino-2-phenylindole. It is easily converted, by the removal of oxygen, into 3-*iso*nitroso-2-phenylindole, $C_6H_4{<}\begin{matrix}C(NOH)\\N\end{matrix}{>}CPh$, and can be oxidised to a *substance* $C_{14}H_9O_2N$, which sublimes in lustrous

red plates, has the properties of a quinone, and possibly is to be represented by the formula $C_6H_4<\genfrac{}{}{0pt}{}{CO}{NO}>NPh$, since with hydroxylamine it gives *iso*nitrosophenylindole. W. A. D.

A New Class of Dyes obtained from Quinoline-2-carboxylic Acids. Emil Besthorn and J. Ibele (*Ber.*, 1904, **37**, 1236—1243).—When quinoline-2-carboxylic acid is heated with acetic anhydride for half an hour at 130—135°, a *substance* $C_{19}H_{12}ON_2$ is obtained which crystallises from absolute alcohol in red, pleochroic needles, sinters at 200°, and melts indefinitely at 230—240°; in solution, it is fluorescent and remarkably sensitive to light, the colour of a saturated benzene solution disappearing when exposed to bright sunshine in a few minutes. The composition of the substance would correspond with that of a 2:2′-*diquinolyl ketone*, $CO(C_9H_6N)_2$, and in agreement with this structure it is converted by boiling hydrobromic acid into quinoline and quinoline-2-carboxylic acid, and by sulphuric acid into quinoline-2-carboxylic acid and carbostyril; on the other hand, it is a feeble base, and does not interact with hydroxylamine or phenylhydrazine. Attempts to prepare 2:2′-diquinolyl ketone by heating calcium quinoline-2-carboxylate gave only 2 : 7′-diquinolyl.

The same substance, $C_{19}H_{12}ON_2$, is also formed on heating quinoline-2-carboxylic acid with benzoic anhydride at 140°, but anhydrides of dibasic acids, such as phthalic or succinic anhydrides, act differently. W. A. D.

4-Quinolylacrylic Acid and 4-Quinolylpropionic Acid. Wilhelm Koenigs and Alfred Müller (*Ber.*, 1904, **37**, 1337—1340).—Alcoholic potassium hydroxide converts chloral-lepidine into *quinolyl*-4-*acrylic acid*, $C_9NH_6\cdot CH\colon CH\cdot CO_2H$, which crystallises from a mixture of alcohol and acetic acid in small, white needles and melts and decomposes at 250—255°. The *hydrochloride* forms long, felted needles. The *platinichloride* forms yellow needles containing $1\frac{1}{2}H_2O$ and becomes anhydrous at 120°.

Hydriodic acid reduces quinolyl-4-acrylic to *quinolyl*-4-*propionic acid*, $C_9NH_6\cdot CH_2\cdot CH_2\cdot CO_2H$, which crystallises from water in white needles, melts at 202—203°, and dissolves readily in alcohol or hot acetone. The *copper* salt forms characteristic violet-blue crystals. The *platinichloride* forms yellow tablets.

Sodium reduces the alcoholic solution of 4-quinolylpropionic acid to 4-*tetrahydroquinolylpropionic acid*, which darkens in the air and melts at 217—218°. The *nitroso*-compound, $NO\cdot C_9NH_9\cdot CH_2\cdot CH_2\cdot CO_2H$, crystallises from ether in faintly yellow cubes, melts and decomposes at 121—122°, and dissolves readily in ether or alcohol. C. H. D.

Derivatives of 2:4-Dimethylquinoline and 2:4:6-Trimethylpyridine. Wilhelm Koenigs and Alfred Mengel (*Ber.*, 1904, **37**, 1322—1337).—Acetylacetone anilide, described by Coombes (Abstr., 1888, 504) as a liquid, crystallises from light petroleum in colourless leaflets, melts at 51—53°, and boils at 279—281° (uncorr.) under 715 mm. pressure. Concentrated sulphuric acid converts it into 2 : 4-dimethylquinoline.

Formaldehyde reacts with an excess of 2 : 4-dimethylquinoline to form 4-*methyl-2-β-hydroxyethylquinoline*, $OH\cdot C_2H_4\cdot C_9NH_5Me$, separating from ethyl acetate in white crystals and melting at 98°. The *hydrochloride* is anhydrous and melts at 193—194°, the *platinichloride* forms orange needles and melts and decomposes at 210—211°, the *picrate* forms small, yellow needles and melts at 164—166°. Nitric acid oxidises the base to 4-*methylquinoline-2-carboxylic acid*, separating from water as a crystalline, yellow powder containing $1\frac{1}{2}H_2O$, which is evolved at 105°, the acid then melting at 153—154°. The *platinichloride* forms yellowish-red crystals containing H_2O, blackens at 200°, and melts and decomposes at 210—212°. The *hydrogen sulphate* and *hydrochloride* form white crystals. The readily soluble ammonium salt separates from water in large, feathery crystals. The acid decomposes into carbon dioxide and lepidine at 170—180°.

2 : 4-Dimethylquinoline and formaldehyde also react to form 4-*methyl-2-αγ-dihydroxy*iso*propylquinoline*, $CH(CH_2\cdot OH)_2\cdot C_9NH_5Me$, crystallising from ethyl acetate in slender needles, sintering at 135°, and melting at 140°. The *hydrochloride* forms a white, crystalline powder and melts at 194°, the *platinichloride* forms reddish-yellow needles containing H_2O, becomes anhydrous at 110—120°, and melts and decomposes at 172°.

No higher condensation product with formaldehyde could be obtained in a crystalline condition.

Chloral-2 : 4-*dimethylquinoline*, $CCl_3\cdot CH(OH)\cdot CH_2\cdot C_9NH_5Me$, from chloral and dimethylquinoline in amyl acetate solution, forms colourless crystals and melts at 126°. The sparingly soluble *hydrochloride* melts at 154°. Alcoholic potassium hydroxide converts the base into 4-*methylquinoline-2-acrylic acid*, $C_9NH_5Me\cdot CH{:}CH\cdot CO_2H$, crystallising from alcohol in slender, yellow needles and melting at 214°. The *platinichloride* forms reddish-yellow needles and melts above 300°. Potassium permanganate oxidises 4-methylquinoline-2-acrylic acid to 4-methylquinoline-2-carboxylic acid and oxalic acid.

Acetylacetone-p-*anisidide* crystallises from light petroleum in white tablets and melts at 49°. It was not found possible to convert it into the corresponding quinoline derivative by means of dehydrating agents.

5-*Methoxy*-2 : 4-*dimethylquinoline* is best prepared by condensing paraldehyde with acetone by means of hydrogen chloride and combining the product with *p*-anisidine. It crystallises in colourless needles containing $2H_2O$ and melts at 92°. The *picrate* forms felted, yellow needles and melts at 221°, the *platinichloride* forms orange needles and melts at 241°, the *sulphate* forms slender needles and melts and decomposes at 242°, the *chromate* forms brown needles and decomposes at 188° without melting. The solution of the base in very dilute sulphuric acid shows a strong blue fluorescence, and gives a green coloration with chlorine water and ammonia. The *phthalone* crystallises from alcohol in reddish-yellow needles and melts at 272°.

Chloral-2 : 4 : 6-*trimethylpyridine* (chloral-collidine) crystallises from acetone and melts at 139·5°. A condensation product with more than 1 mol. of chloral could not be prepared. C. H. D.

4-Hydroxy*iso*carbostyril. ARTHUR ULRICH (*Ber.*, 1904, 37, 1685—1696. Compare Abstr., 1900, i, 359).—*a-Phthalyliminophenylacetic acid*, $C_8H_4O_2{:}N{\cdot}CHPh{\cdot}CO_2H$, prepared by the action of phthalic anhydride on aminophenylacetic acid, crystallises in pointed, rhombic leaflets and melts at 168°. The *ethyl* ester crystallises in ball-like aggregates of colourless leaflets, melts at 99°, and by sodium methoxide is converted into 4-hydroxy-3-phenyl*iso*carbostyril,

$$C_6H_4<\begin{matrix}CO\text{——}NH\\ C(OH){:}CPh\end{matrix}$$

(Gabriel, Abstr., 1886, 266; 1887, 61), which is reduced by hydriodic acid and phosphorus at 190° to phenyl*iso*carbostyril. *a-Phthaloylaminophenylacetic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CHPh{\cdot}CO_2H$, is formed by the action of sodium methoxide on ethyl a-phthalylaminophenylacetate in aqueous-alcoholic solution. 4-Methoxy-3-phenyl*iso*carbostyril (Gabriel, *Ber.*, 1887, 20, 2867), formed by the action of sodium methoxide and methyl iodide in methyl-alcoholic solution on 4-hydroxy-3-phenyl*iso*carbostyril, melts at 240° and is reconverted into hydroxyphenyl*iso*carbostyril by the action of boiling hydrobromic acid. 1-*Chloro*-4-*hydroxy*-3-*phenyl*iso*quinoline*,

$$C_6H_4<\begin{matrix}CCl\text{==}N\\ C(OH){:}CPh\end{matrix},$$

is formed along with a small quantity of 1 : 4-*dichloro*-3-*phenyl*iso*quinoline* by the action of phosphorus oxychloride on 4-hydroxy-3-phenyl*iso*carbostyril at 150—160°. It crystallises in transparent prisms, melts at 119°, is soluble in dilute cold aqueous potassium or sodium hydroxide solutions, but not in dilute ammonia.

1-*Chloro*-4-*methoxy*-3-*phenyl*iso*quinoline*, $C_6H_4<\begin{matrix}CCl\text{=}N\\ C(OMe)\end{matrix}>CPh$, is formed by the action of phosphorus oxychloride on 4-methoxy-3-phenyl*iso*carbostyril, and by the action of methyl iodide and sodium methoxide on 1-chloro-4-hydroxy-3-phenyl*iso*quinoline. It crystallises in prisms, melts at 103·5°, and is isomeric with 4-chloro-1-methoxy-3-phenyl*iso*quinoline, which melts at 76° (Gabriel, Abstr., 1887, 61).

4-*Ethoxy*-3-*phenyl*iso*carbostyril* crystallises in stellate clusters of rose-coloured needles and melts at 183°. 1-*Chloro*-4-*ethoxy*-3-*phenyl*iso*quinoline* melts at 83·25°.

4-*Methoxy*-3-*ethyl*iso*carbostyril*, $C_6H_4<\begin{matrix}CO{\cdot}NH\\ C(OMe)\end{matrix}>CEt$, obtained from 4-hydroxy-3-ethyl*iso*carbostyril (Abstr., 1900, i, 359), crystallises in stellate clusters of needles and melts at 160—160·5°. 1-*Chloro*-4-*methoxy*-3-*ethyl*iso*quinoline* crystallises in colourless, hexagonal leaflets and melts at 55·5°. 1-*Chloro*-4-*hydroxy*-3-*ethyl*iso*quinoline* crystallises in clusters of quadratic prisms and melts at 125·25°.

Ethyl a-phthalyliminoisovalerate, $C_8H_4O_2{:}N{\cdot}CH(CHMe_2){\cdot}CO_2Et$, prepared by the action of potassium phthalimide on ethyl a-bromo*iso*valerate, is a yellow liquid, which boils at 211° under 36·6 mm. pressure. Sodium methoxide converts it into 4-*hydroxy*-3-iso*propyl*iso*carbostyril*, $C_6H_4<\begin{matrix}CO\text{——}NH\\ C(OH){:}CPr^{\beta}\end{matrix}$, which crystallises in colourless

tetrahedra and melts at 198—207°. It is soluble in dilute sodium hydroxide solution, from which it is precipitated by ammonium chloride or hydrochloric acid. *a-Phthalyliminoisohexoic acid,*

$$C_8H_4O_2{:}N{\cdot}CH(C_4H_9){\cdot}CO_2H,$$

is formed by the action of phthalic anhydride on leucine. It crystallises in rhombic leaflets and melts at 141·5—142°. The *methyl* ester melts at 65·5—66°, and, when acted on by sodium methoxide, yields 4-*hydroxy*-3-iso*butyl*iso*carbostyril*, which melts at 171—173°. G. Y.

Combination of *o*-Nitrobenzaldehyde with Phenol in presence of Hydrochloric Acid. ALFRED GUYOT and ALBERT HALLER (*Bull. Soc. chim.*, 1904, 31, 530—533).—When a mixture of *o*-nitrobenzaldehyde and phenol, dissolved in acetic acid, is heated at 100° with hydrochloric acid, a *product* $C_{13}H_8O_2NCl$ is formed, which may have the constitution $C_6H_3Cl{<}{}^{NH}_{CO}{>}C_6H_3{\cdot}OH$. It is crystalline, melts and sublimes at 200°, and is soluble in alcohol. On the addition of a drop of alkali to its alcoholic solution, a magnificent green fluorescence is produced. With silver nitrate, followed by a drop of ammonia, the alcoholic solution gives a crystalline, vermilion-coloured precipitate of the *silver* derivative. The *methyl ether*, obtained by the action of methyl iodide in closed tubes at 100°, crystallises in long, yellow needles and melts at 144°; the *benzyl ether*, produced by warming alkaline solutions of the condensation product with benzyl chloride, forms fine crystals and melts at 142°; the *benzoyl* derivative occurs in small crystals and melts at 231°.

This condensation product has also been described by Siebert (*Inaug. Diss. Marburg*, July, 1903), who ascribed to it the formula

$$C_6H_3Cl{<}{}^{C\text{——}C_6H_4\cdot OH}_{N}{>}O.$$

T. A. H.

Preparation of Acridine Dyes. ANILINFARBEN- and EXTRAKT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 149409 and 149410).—Orange-yellow dyes of the acridine series are obtained by heating formyl derivatives of *m*-diamines (Abstr., 1903, i, 522) or the formyl derivatives of aromatic amines and alkylated amines, and many other formyl derivatives of aromatic bases, with ammonium salts or salts of organic bases at 150—200°. The salts appear to act only as condensing agents, and their nature is without effect on the character of the product. The solutions of the dyes in water, alcohol, or concentrated sulphuric acid are fluorescent, but less so than solutions of acridine yellow. C. H. D.

A New Base from *p*-Phenylenediamine. LUDWIG PAUL (*Zeit. angew. Chem.*, 1904, 17, 589—591).—The author endeavours to ascertain the conditions under which the base previously prepared by him from impure *p*-phenylenediamine (*ibid.*, 1897, 10) may be prepared from pure *p*-phenylenediamine. A. McK.

Chloronitro- and Nitro-derivatives of 4-Hydroxy-2′:4′-dinitrodiphenylamine. FRÉDÉRIC REVERDIN and ERNST DELÉTRA (*Ber.*, 1904, 37, 1727—1732. Compare Abstr., 1903, i, 248, 857).—3:2′:4′-*Trinitro-4-aminodiphenylamine*, obtained from 1-chloro-2:4-

dinitrobenzene and *o*-nitro-*p*-phenylenediamine, crystallises in small, reddish-brown needles, melts at 226°, and is probably identical with the base described by the Farbwerke Höchst (D.R.-P. 1899, 110360). When treated with sodium chlorate and hydrochloric acid, it yields the 2 : 3 : 5- or 2 : 3 : 6-trichloroquinone-2′ : 4′-dinitrophenylimide, which melts at 211°, together with a *tetrachloroquinone*-2′ : 4′-*dinitrophenylimide.*

3-*Chloro*-2 (or 6) : 2′ : 4′-*trinitro*-4-*acetoxydiphenylamine*,

$$OAc\cdot C_6H_2Cl(NO_2)\cdot NH\cdot C_6H_3(NO_2)_2,$$

is obtained by acting with fuming nitric acid on 3-chloro-2′ : 4′-dinitro-4-acetoxydiphenylamine. It crystallises in needles, melts at 177·5—178°, and is hydrolysed to 3-*chloro*-2 (or 6) : 2′ : 4′-*trinitro*-4-*hydroxydiphenylamine*, which melts at 252°.

3-*Chloro*-2′ : 4′ : 6′-*trinitro*-4-*hydroxydiphenylamine*,

$$OH\cdot C_6H_3Cl\cdot NH\cdot C_6H_2(NO_2)_3,$$

obtained from 2-chloro-4-aminophenol and picryl chloride, forms dark red, prismatic crystals and melts at 185·5°. The *acetyl* derivative crystallises in orange-coloured prisms and melts at 173°.

3-*Chloro*-5 : 2′ : 4′-*trinitro*-4-*hydroxydiphenylamine*,

$$OH\cdot C_6H_2Cl(NO_2)\cdot NH\cdot C_6H_3(NO_2)_2,$$

obtained from 2-chloro-6-nitro-4-aminophenol (D.R.-P. 1903, 11458) and chlorodinitrobenzene, crystallises in matted, golden needles and melts at 232°. The *acetyl* derivative crystallises in brown prisms and melts at 188·5°.

2-Chloro-2′ : 4′-dinitro-4-acetoxydiphenylamine yields a *mononitro*-derivative, $OAc\cdot C_6H_2Cl(NO_2)\cdot NH\cdot C_6H_3(NO_2)_2$, which crystallises from acetone in lemon-yellow prisms, containing acetone of crystallisation, and after heating at 100° melts at 134·5°. On hydrolysis with sodium hydroxide, a gelatinous *sodium* derivative is formed, which, with hydrochloric acid, yields *nitro-2-chloro-2′* : 4′-*dinitro*-4-*hydroxydiphenylamine*. This crystallises in yellow, prismatic needles and melts at 232·5°.

3 : 5-Dichloro-2′ : 4′-dinitro-4-acetoxydiphenylamine yields a *mononitro*-derivative which melts at 177·5°; the corresponding *hydroxy*-compound, $OH\cdot C_6H_4Cl_2\cdot NH\cdot C_6H_3(NO_2)_2$, crystallises in orange-coloured prisms and melts at 235°; the *sodium* derivative forms glistening, red leaflets.

3 : 5-*Dichloro*-2′ : 4′ : 6′-*trinitro*-4-*hydroxydiphenylamine*, obtained from picryl chloride and 2 : 6-dichloro-4-aminophenol, crystallises in glistening, brown prisms and melts at 225°. The *acetyl* derivative forms greenish-yellow leaflets and melts at 259°.

Dinitro-2′ : 4′-dinitro-4-acetoxydiphenylamine,

$$OAc\cdot C_6H_2(NO_2)_2\cdot NH\cdot C_6H_3(NO_2)_2,$$

obtained by nitration of 2′ : 4′-dinitro-4-acetoxydiphenylamine, crystallises in large, brownish-yellow prisms or yellow needles and melts at 161°; the *hydroxy*-compound crystallises in lemon-yellow needles and melts at 225·5°; the *sodium* compound is gelatinous. The same dinitro-2′ : 4′-dinitro-4-hydroxydiphenylamine is obtained by successive nitration and hydrolysis of the dinitrophenyl ether or the *p*-tolylsulphonate of 2′ : 4′-dinitro-4-hydroxydiphenylamine. The p-*tolylsulphonate*,

$$C_7H_7\cdot SO_3\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2,$$

obtained from *p*-tolylsulphonic chloride and 2′ : 4′-dinitro-4-hydroxy-

diphenylamine, crystallises in yellow leaflets or prismatic needles and melts at 178·5°. On nitration, it yields a *dinitro*-derivative,

$$C_7H_7\cdot SO_3\cdot C_6H_2(NO_2)_2\cdot NH\cdot C_6H_3(NO_2)_2,$$

which crystallises in delicate, lemon-yellow needles and melts at 189·5°. The *dinitro*-derivative of the dinitrophenyl ether of 2′ : 4′-dinitro-4-hydroxydiphenylamine crystallises in brownish-yellow leaflets and melts at 233°. G. Y.

Tolylenediaminesulphonic Acids. CARL BÜCKEL (*Zeit. Farb. Text. Chem.*, 1904, 3, 137—139).—The acid obtained by Wiesinger (this Journ., 1874, 805) on sulphonating *m*-tolylenediamine is shown to be identical with Foth's acid (Abstr., 1886, 152), prepared from *o*-nitro-*p*-toluidine; it has therefore the structure $[Me:(NH_2)_2:SO_3H = 1:2:4:5]$.

The acid $[Me:(NH_2)_2:SO_3H = 1:2:4:6]$ mentioned in Oehler's Patent (D.R.-P. 51662) is prepared by nitrating with a mixture of fuming nitric and sulphuric acids the acid obtained on sulphonating *p*-nitrotoluene, and subsequently reducing the dinitrotoluenesulphonic acid with zinc and hydrochloric acid; the *hydrochloride* of the diaminotoluenesulphonic acid crystallises from water, but is gradually dissociated by repeated crystallisation, forming the sulphonic acid itself.

The acid $[Me:(NH_2)_2:SO_3H = 1:2:6:4]$ is best obtained by Schwanert's method (this Journ., 1877, ii, 471). The three acids are distinguished by the nature of the azo-dyes they give with diazotised *p*-toluidine, *o*-toluidine, and *o*-tolidine. For details, the original should be consulted. W. A. D.

Constitution of *o*-Tolidine. GUSTAV SCHULTZ, GEORG ROHDE, and F. VICARI (*Ber.*, 1904, 37, 1401—1402).—The hydrocarbon obtained by the elimination of the amino-groups from *o*-tolidine is identical with the compound obtained by the action of sodium on *m*-iodotoluene, and must therefore be 3 : 3′-dimethyldiphenyl; the constitution of *o*-tolidine, therefore, is $NH_2\cdot C{<}{}^{CMe:CH}_{CH-CH}{>}C\cdot C{<}{}^{CH:CMe}_{CH-CH}{>}C\cdot NH_2$.

J. J. S.

Some Amino- and Aminohydroxy-diphenylamines. ROBERT GNEHM [with G. WEBER] (*J. pr. Chem.*, 1904, [ii], 69, 223—244).—Dimethyl-*p*-diaminodiphenylamine (Abstr., 1903, i, 831) can also be prepared by heating dimethyl-*p*-phenylenediamine with *p*-aminophenol and a little zinc chloride at 150° in an atmosphere of carbon dioxide; its *hydrochloride*, $C_{14}H_{17}N_3,2HCl$, and *sulphate*, $C_{14}H_{17}N_3,H_2SO_4$, were analysed; it forms a *triacetyl* derivative, melting at 142°. When boiled in alcoholic solution with 1-chloro-2 : 4-dinitrobenzene and sodium acetate, it yields a condensation *product*, $C_{20}H_{19}O_4N_5$, melting at 209°. When added gradually to a mixture of sulphur and phenol heated at 200—250°, it forms an amorphous sulphuretted *colouring-matter*.

Dimethyltriaminodiphenylamine, $NMe_2\cdot C_6H_4\cdot NH\cdot C_6H_3(NH_2)_2$, is obtained by reducing *p*-nitrosodimethylaniline hydrochloride in aqueous solution with zinc dust, adding *m*-phenylenediamine, oxidising with sodium hypochlorite solution at 0°, filtering off the indamine which is

precipitated, and reducing it in solution in dilute acetic acid with zinc dust; it crystallises with difficulty, melts at 70—75°, oxidises readily in the air, and yields a sulphuretted *colouring-matter.*

Dimethyl-*p*-amino-*m*-hydroxydiphenylamine (*loc. cit.*) forms a *hydrochloride,* $C_{14}H_{16}ON_2,HCl$, melting at 207°, and a *sulphate,*

$$2C_{14}H_{16}ON_2,H_2SO_4,$$

melting at 193°; when boiled with methyl iodide and sodium hydroxide in methyl alcoholic solution, it forms a *methiodide,* $C_{14}H_{16}ON_2,MeI$, which melts at 199·5—200°; the *ethiodide* melts at 180°. The nitrosoamine, when allowed to remain with alcoholic hydrochloric acid at 0°, becomes transformed into reddish-brown p-*nitrosodimethyl*-p-*amino*-m-*hydroxydiphenylamine,* $C_{14}H_{15}O_2N_3$, melting at 164°; this is reduced by alcoholic ammonium sulphide to the corresponding *amine,* $C_{14}H_{17}ON_3$, and with *p*-nitrobenzyl cyanide, it yields a reddish-brown *azomethine* derivative, $C_{22}H_{19}O_3N_5$, melting at 213—214°. With formaldehyde, 1 mol. of the original base condenses in alcoholic hydrochloric acid solution to amorphous *dimethyl*-p-*aminophenylamino*-m-*hydroxybenzyl alcohol,* $NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}OH$, which does not melt at 360°; 2 mols. condense to amorphous *tetramethyl*-p-*diamino*-p-*diphenyl*-p-*diamino*-m-*dihydroxydiphenylmethane,*

$$CH_2[C_6H_3(OH){\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2]_2,$$

melting at about 150°, which, when oxidised together with dimethylaniline in acid solution, yields a green triphenylmethane *dye,* $C_{29}H_{32}O_2N_4$. The original base yields a sulphuretted *colouring-matter.*

2-*p*-Dimethylanilino-7-hydroxynaphthalene (*loc. cit.*) forms a *diacetyl* derivative melting at 100° when it is shaken in ethereal solution with acetyl chloride and dry potassium carbonate; when it is boiled with acetic anhydride, the diacetyl derivative of 2 : 7-dihydroxynaphthalene is formed. C. F. B.

Ethyl Bisdiazoacetoacetate. MARIO BETTI (*Gazzetta,* 1904, 34, i, 179—194. Compare Abstr., 1903, i, 78).—On hydrolysis with dilute hydrochloric or sulphuric acid, ethyl bisdiazoacetoacetate yields (1) ethylnitrosoacetoacetate, which undergoes further change into oxides of nitrogen, alcohol, carbon dioxide, acetone, acetic acid, &c., and (2) a *substance,* $CO_2Et{\cdot}CHAc{\cdot}N{:}N{\cdot}NH_2$, which becomes resolved into alcohol and iso*nitrosomethylpyrazolone,* $NH<\begin{matrix}CO{\cdot}C{:}N{\cdot}OH\\ N{=\!=}CMe\end{matrix}$, which separates in massive, yellow needles, melts and decomposes at 230°, and is soluble in alcohol or water; it is a monobasic acid, and with alkali hydroxides gives a scarlet coloration. Its *sodium* salt, $C_4H_4O_2N_3Na$, which is deposited from dilute alcohol in golden-yellow crystals, decomposes without melting at above 250° and dissolves readily in water; the aqueous solution gives coloured precipitates with salts of the heavy metals. It has the normal molecular weight in boiling alcohol. Its *benzoyl* derivative, $C_4H_4O_2N_3Bz$, crystallises from alcohol in long, silky needles melting and decomposing at 170—180°. On oxidation with nitric acid, it gives a *compound,* $NH<\begin{matrix}CO{\cdot}CH{\cdot}NO_2\\ N{=\!=}CMe\end{matrix}$, separating from acetic acid in shining, white crystals which melt at 276° and are

slightly soluble in ethyl or amyl alcohol or acetone. When reduced with zinc dust and dilute hydrochloric acid, it is converted into the corresponding amino-base, which, in the air, immediately becomes changed into a *compound*, $\begin{matrix} NH\cdot CO \\ \vert \\ N:CMe \end{matrix}\!>CH\cdot N:C<\!\begin{matrix} CO-NH \\ \vert \\ CMe:N \end{matrix}$, which decomposes, without melting, at above 250°.

*iso*Nitrosomethylpyrazolone may also be prepared by the action of nitrous acid on methylpyrazolone. T. H. P.

Indophthalone. CARL RENZ (*Ber.*, 1904, 37, 1221—1225).—Phthalyl chloride condenses with 2-methylindole (2 mols.) at 150—160° giving *indophthalone hydrochloride*, $C_{26}H_{20}O_2N_2,HCl$, which forms a red powder, melts at 272—273°, and cannot be recrystallised; when decomposed with aqueous sodium carbonate, it gives *indophthalone*, $C_{26}H_{20}O_2N_2$, as a vermilion-coloured precipitate melting at 212°, and yielding a *potassium* derivative which crystallises in golden leaflets.

When 2-methylindole (2 mols.) is heated with phthalic anhydride in a sealed tube at 150°, the same acid, $C_9H_8N\cdot CO\cdot C_6H_4\cdot CO_2H$, is formed as was obtained by Fischer (Abstr., 1887, 265) in the case of molecular quantities at 100°; when, however, the mixture of the two substances (2 : 1) is heated in an open vessel at 185—190°, indophthalone is formed, which can be isolated as the hydrochloride (m. p. 265°). The yield in this case is small, so that it cannot be established whether the phthalone exists in two isomeric forms. W. A. D.

Constitution of the Basic Triphenylmethane Dyes. HUGO KAUFFMANN (*Zeit. Farb. Text. Chem.*, 1904, 3, 117—118).—Controversial. The author considers von Georgievics' formula (this vol., i, 351) for the triphenylmethane dyes unnecessary, the commonly accepted constitution explaining all the facts. W. A. D.

Preparation of Aromatic Substituted Guanidine from Cyanamide. ADOLF KÄMPF (*Ber.*, 1904, 37, 1681—1684).—The action of aniline hydrochloride or nitrate on cyanamide in absolute alcoholic solution leads to the formation of phenylguanidine hydrochloride or nitrate respectively. On evaporation, the hydrochloride is obtained as a yellow syrup, the nitrate in thick prisms which melt at 128°. Phenylguanidine, liberated from its hydrochloride by the action of silver oxide in aqueous solution, forms crystals which persistently retain the last traces of water and melt at 50—60°. The picrate melts at 221—222° (compare Prelinger, Abstr., 1892, 950). With silver chloride, phenylguanidine forms an insoluble compound which yields phenylguanidine nitrate when acted on by nitric acid. *Dibenzoylphenylguanidine*, formed from the nitrate by the Schotten-Baumann method, melts at 187°, is only slightly soluble in most solvents, and on nitration yields *p*-nitrobenzoic acid. p-*Tolylguanidine nitrate*, obtained by acting with *p*-toluidine nitrate on cyanamide, melts at 146—147° and is easily soluble in alcohol, glacial acetic acid, or acetone. *p*-Tolylguanidine, precipitated as a white mass on addition of potassium hydroxide to the nitrate in aqueous solution, is easily soluble in ether.

Nitrophenylguanidines are not formed by the action of the sulphates, nitrates, or oxalates of *o*- or *p*-nitroaniline. This the author considers to be due to the complete dissociation of these salts in solution. The action of the oxalates in presence of water leads to the formation of carbamide oxalate, which melts at 170—171°.

When boiled in a reflux apparatus in absolute alcoholic solution, silver cyanamide and phenylthiocarbimide react to form the *imino-ether* of phenylcyanocarbodi-imide, NHPh·C(OEt)⁚N·CN, which crystallises in white needles, melts at 126—127°, and is easily soluble in the ordinary solvents. With absolute alcoholic ammonia at 100° under pressure, the imino-ether yields a *substance* which melts at about 170° and has the composition C = 40·12, H = 5·01, N = 50·33 per cent. With aniline, the imino-ether yields *s*-diphenylcarbamide. G. Y.

Additive Compounds of Acids with Azo-compounds and with αβ-Unsaturated Ketones at Low Temperatures. DANIEL VORLÄNDER and C. TUBANDT (*Ber.*, 1904, **37**, 1644—1654. Compare Abstr., 1903, i, 495; this vol., i, 65).—Unsaturated ketones are as readily coloured by melting hydrogen bromide at −87° or by melting hydrogen chloride at −112° as by the same compounds at the ordinary temperature. Comparative experiments on the percentage of hydrogen chloride (as HCl, *A*) contained in the solid additive compounds at different temperatures have proved that the percentage is much higher at low temperatures; for example, the additive compound of dibenzylidene acetone contains 42 per cent. of hydrogen chloride at −76°, but only 22—23 at −20° or +18°.

When, however, the hydrogen chloride combines to form the *B* compound, the velocity of addition falls with the temperature.

Azobenzene, aminoazobenzene, dimethylaminoazobenzene, acetyl- and benzoyl-aminoazobenzenes, azobenzenetrimethylammonium chloride or bromide form monohydrochlorides with characteristic orange, red, or violet-red colours. These compounds react with hydrogen chloride at −75° to −77°, yielding pale yellow-coloured polyhydrochlorides, which lose hydrogen chloride as the temperature is allowed to rise, and at 15° the highly coloured mono- or bis-hydrochlorides are formed.

Corresponding hydrobromides have been obtained: they are somewhat deeper in colour than the hydrochlorides, and the hydrogen bromide is added on more readily than the chloride, so that at 0° or −20° polyhydrobromides are obtained.

The hydrobromide *B* of dibenzylideneacetone is more readily formed by the action of hydrogen bromide on the ketone itself than on the hydrobromide *A* at the same temperature.

Benzylideneacetophenone hydrobromide *B* melts at about 110°, and when crystallised from warm glacial acetic acid is decomposed into its components.

The following general conclusions are drawn:

(1) The additive reactions between acids and unsaturated compounds (amines, ketones, esters, salts, &c.) are quite different from processes of neutralisation of an acid by a base with elimination of water.

(2) Opposed to the addition is a process of dissociation into acid and

the unsaturated compound. This is often confused, when it occurs in aqueous or alcoholic solution, with hydrolysis or alcoholysis.

(3) The addition and dissociation are dependent on the composition of the components, on any third substance which may be present, on temperature, pressure, light, &c.

(4) A component is capable of displacing another from an additive compound, but the reaction is much slower than when the two components combine directly.

(5) The same unsaturated compound can give rise to isomeric additive products with the same acid. This phenomenon is termed additive isomerism, and cannot be explained by the ordinary theories of valency or ionisation. J. J. S.

Solid Solutions and Isomorphism. GIUSEPPE BRUNI (*Gazzetta*, 1904, 34, i, 144—146. Compare Bruni and Gorni, Abstr., 1899, ii, 731; 1900, ii, 714; and Garelli and Calzolari, Abstr., 1899, ii, 732). —[With BILLOWS.]—*p*-Azotoluene crystallises in the monoclinic system [$a:b:c=0\cdot5687:1:1\cdot7105$; $\beta=89°44'$]. *p*-Hydrazotoluene also forms monoclinic crystals [$a:b:c=0\cdot6279:1:2\cdot0286$; $\beta=89°49'$]. T. H. P.

The so-called Diazosulphonaphtholsulphonic Acids of the German Patent 121226. HANS BUCHERER (*Zeit. Farb. Text. Chem.*, 1904, 3, 118—120).—The compounds obtained by the action of sulphites on diazotised β-naphthylamine-5:7- and -8:6-disulphonic acids are apparently neither dihydroxyazonaphthalenedisulphonic acids nor diazosulphonaphtholsulphonic acids (compare Hantzsch, Abstr., 1897, i, 185); they do not possess the tinctorial qualities of the former, neither are they reducible, like the latter substances, to hydroxynaphthylhydrazinesulphonic acids or the naphthylaminesulphonic acids from which they are derived. Their nature remains to be more fully investigated. W. A. D.

Electrolytic Preparation of Azo-dyes. WALTHER LÖB (*Zeit. Elektrochem.*, 1904, 10, 237—238).—When a solution containing an aromatic amine and sodium nitrite is electrolysed with a platinum anode, it is probable that a diazo-compound is formed. It is not possible, however, to isolate it. When a phenol is added to the solution, it combines with the diazo-compound before it can be changed in any other way, and the corresponding dye is produced. The materials are used in molecular proportions, the phenol being preferably in a soluble form and the anode compartment in which the reaction occurs is separated from the cathode by a porous diaphragm. From 0·005 to 0·06 ampere per sq. cm. may be used, and it is unnecessary to cool the solutions below the ordinary temperature. T. E.

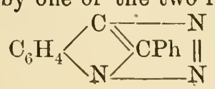
[Azo-dyes from 1-Chloro-2:6-diaminobenzene-4-sulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 150373).—1-*Chloro*-2:6-*diaminobenzene*-4-*sulphonic acid*, prepared by reducing chlorodinitrobenzenesulphonic acid (D.R.-P. 116759) with tin and

hydrochloric acid, forms colourless needles containing H_2O, insoluble in water, soluble in dilute alkalis, and reprecipitated by acids. Nitrous acid forms a yellow tetrazo-compound, which combines with naphthols and their sulphonic acids to form azo-dyes, which are free from chlorine and are identical with those prepared from diaminophenol-sulphonic acid. The chlorine atom has therefore been replaced by the hydroxyl group. C. H. D.

Azo-dye from 4-Acetyl-2 : 4-diaminophenol-6-sulphonic Acid. Leopold Cassella & Co. (D.R.-P. 149106).—*4-Acetyl-2 : 4-diaminophenol-6-sulphonic acid*, prepared from acetyl-*p*-aminophenol by sulphonation, nitration, and reduction, yields a soluble, yellow diazonium compound, which combines with β-naphthol to form a claret-coloured dye, which becomes black on subsequent treatment with an alkali chromate. C. H. D.

Diazoamino-compounds of Aminonaphtholsulphonic Acids. Ludwig Paul (*Zeit. angew. Chem.*, 1904, **17**, 363—365).—When the tetrazo-derivative of tolidine is added to an aqueous solution of aminonaphtholdisulphonic acid-H, a slight precipitate is formed if the latter acid contains some monosulphonic acid. The filtrate contains a diazoamino-compound, and addition of *p*-nitrodiazobenzene causes a voluminous, bluish-red precipitate, which, when introduced in the pasty condition into a concentrated solution of sodium salicylate or of sodium phenoxide, forms the monoazo-dye of *p*-nitrodiazobenzene and aminonaphtholdisulphonic acid-H on the one hand, and the intermediate compound of tetrazoditolyl and phenol (or salicylic acid) on the other. When the precipitate, however, is well washed with water, it is transformed into the bluish-green aminoazo-compound. The sodium salt of aminonaphtholsulphonic acid-γ in combination with tetrazoditolyl also forms a diazoamino-compound which interacts with *p*-nitrodiazobenzene. When molecular amounts of tetrazoditolyl and sodium β-naphtholdisulphonate-γ are united in moderately dilute aqueous solution, flesh-coloured leaflets quickly separate, which alkali changes into a red compound. The intermediate compound is converted by sodium hydrogen sulphite into a substance which is not a dye. A. McK.

Diazoindoles. Angelo Angeli and Antonino D'Angelo (*Atti R. Accad. Lincei*, 1904, [v], **13**, i, 258—259).—3-Amino-2-phenylindole, on treatment with nitrous acid, is converted into a substance, $C_{14}H_9N_3$, which crystallises from light petroleum in orange-yellow prisms, melts at 115°, and appears to be the anhydride of a diazohydroxide, $C_6H_4{<}\begin{matrix}C(N_2\cdot OH)\\ NH\end{matrix}{>}CPh$. The structure would thus be represented by one of the two formulæ,

 or $C_6H_4{<}\begin{matrix}C(:N_2)\\ N\end{matrix}{>}CPh$.

W. A. D.

[Azo-compounds of Phenylmethylpyrazolone.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 150125).—A yellow azo-compound, capable of forming metallic lakes, is obtained by combining diazotised *o*-amino-*p*-sulphobenzoic acid with phenylmethylpyrazolone.
C. H. D.

Diazo-derivatives of Proteids. Z. TREVES and A. PELLIZZA (*Atti R. Accad. Sci. Torino*, 1904, 39, 429—434).—When commercial casein, freed from fat, is treated with nitrous acid in the usual manner of diazotisation, a yellow product is formed which is decomposed by light, alkali hydroxides, or warm concentrated acids in presence of cuprous chloride, with evolution of nitrogen; the yellow mass couples with alkaline β-naphthol, salicylic acid, or amines to form brownish-red azo-compounds. Blood albumin, fibrin, and fish glue show the same behaviour under similar conditions. Fibrin and casein which have been exposed to formaldehyde can still be diazotised, but more slowly, and the product is insoluble in alkali hydroxides. The ordinary diazo-derivatives give the biuret reaction, but when they are obtained from proteid which has been treated with formaldehyde, this is no longer the case. The mode of formation of the diazo-compounds is discussed.
W. A. D.

Formation of Hydrogen Cyanide by the Oxidation of Proteids. R. H. ADERS PLIMMER (*J. Physiol.*, 1904, 31, 65—80).—By the oxidation of proteids with Neumann's acid mixture, hydrogen cyanide is evolved; the amount for each proteid is constant whether it has been hydrolysed or not. The amount varies with different proteids. The amino-acids yield only a small quantity. Oxidation with potassium dichromate and sulphuric acid gives rise to the same amount of the acid, but the yield is small when oxidation is carried out with concentrated sulphuric acid, sulphuric acid and manganese dioxide, or sulphuric acid and potassium permanganate.
W. D. H.

Nucleo-proteids and their Decomposition Products. CARLO FOÀ (*Atti R. Accad. Lincei*, 1904, 13, i, 342—349).—The author's experiments show that the nucleo-proteid of Bang (Abstr., 1900, i, 57) and also that of Huiskamp (Abstr., 1900, ii, 461) are decomposed, by digestion with hydrochloric acid, into an insoluble residue of nuclein, and a proteid substance which remains dissolved in the hydrochloric acid and presents all the reactions of histon. It is not possible to distinguish a nucleo-proteid from a nucleo-histon by the presence in the latter, and the absence from the former, of histon. These two groups of substances should therefore be classed together.
T. H. P.

Hydrolysis of Casein. ZDENKO H. SKRAUP (*Ber.*, 1904, 37, 1596—1597).—A number of new products of hydrolysis have been prepared in crystalline form by an improved method to be described later.

Diaminoglutaric acid forms prisms and melts at 238°, *diaminoadipic*

acid also forms prisms and melts at about 270°. Both acids form soluble, crystalline *copper* salts. Diamino-derivatives of dibasic acids have not hitherto been detected amongst the products of the hydrolysis of proteids.

Many aminohydroxy-acids have been found. *Aminohydroxysuccinic acid* melts at 320°. An *acid*, $C_8H_{16}O_6N_2$, crystallises well and melts at 243°, and is possibly a diaminodihydroxysuberic acid.

Caseanic acid, $C_9H_{16}O_7N_2$, forms very sparingly soluble, characteristic crystals, melts at 192°, and forms an insoluble, bluish-green *copper* salt. The *hydrochloride* crystallises in tablets or long prisms. The acid is tribasic and probably contains one hydroxyl group. *Caseic acid*, $C_{12}H_{16}O_5N_2$, forms a *dextrorotatory* modification crystallising in prisms and melting at 226°, and an *inactive* modification melting at 246°. Both forms yield the same violet *copper* salt and the same *hydrochloride*. C. H. D.

Decomposition Products of Elastin. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1904, **41**, 293—298. Compare Horbaczewski, Abstr., 1883, 927; 1886, 270; Schwarz, 1894, ii, 146; Bergh, 1898, i, 608; Hedin, *ibid.*, 608; Kossel and Kutscher, *ibid.*, i, 718).—The following products have been isolated from elastin after hydrolysis with concentrated hydrochloric acid: glycine, 25·75; leucine, 21·38; alanine, 6·58; phenylalanine, 3·89; pyrrolidine-2-carboxylic acid, 1·74; glutamic acid, 0·76; and aminovaleric acid, 1·0 per cent. J. J. S.

Pigment of the Suprarenal Capsules. C. GESSARD (*Compt. rend.*, 1904, **138**, 586—588). GABRIEL BERTRAND (*ibid.*, 649—650).—The chromogen of this pigment is regarded as the product of the action of tyrosinase on tyrosine. In the second paper, this conclusion is commented on adversely. W. D. H.

Colour Reactions; the Result of the Action of Tyrosinase. C. GESSARD (*Compt. rend.*, 1904, **138**, 774—775. Compare Abstr., 1902, i, 196; 1903, ii, 165).—The action of tyrosinase on tyrosine presents two distinct phases; first a rose-red, then a violet coloration, followed by precipitation of the coloured product. The first phase alone is attributed to ferment action. The chemical nature of the coloured products is as yet undetermined. W. D. H.

Decomposition of Yeast Nucleic Acid by Bacteria. IV. ALFRED SCHITTENHELM and F. SCHRÖTER (*Zeit. physiol. Chem.*, 1904, **41**, 284—292. Compare Abstr., 1903, ii, 679, and this vol., ii, 139).—Among the products obtained by the action of a pure culture of *Bacterium coli* on sodium yeast-nucleate are phosphoric acid, carbon dioxide, formic and oxalic acids, ammonia, alcohol, xanthine, and hypoxanthine. Acetic acid, guanine, and adenine could not be isolated. Probably cytosine and uracil are formed. An acid melting at 183° has also been isolated. J. J. S.

Decomposition Products of Thymus-histon. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1904, 41, 278—283. Compare Kossel and Kutscher, *ibid.*, 1900, 31, 188).—Thymus-histon was hydrolysed with concentrated hydrochloric acid and the products examined by Fischer's esterification method. Among the products isolated were glycine, 0·5; alanine, 3·46; leucine, 11·8; pyrrolidine-2-carboxylic acid, 1·46; phenylalanine, 2·2; glutamic acid, 0·53 per cent. Tyrosine (5·2 per cent.) was also isolated, and indications of the presence of aspartic acid and of cystine were obtained. J. J. S.

Adrenaline [Epinephrine]. II. HERMANN PAULY (*Ber*, 1904, 37, 1388—1401. Compare this vol., i, 128; also Abel, Abstr., 1903, i, 376, 784, and this vol., i, 264, and Jowett, Trans., 1904, 85, 192). —In reply to Abel, experiments have been made to prove that the adrenaline analysed was (*a*) free from organic phosphorus compounds, (*b*) free from adhering ammonia, (*c*) free from water of crystallisation. The formula $C_9H_{13}O_3N$ is retained.

Adrenaline urate, $C_9H_{13}O_3N,C_5H_4O_3N_4$, has been obtained in the form of small, pointed plates. A *dibenzoyl* (?) derivative, $C_9H_{11}O_3NBz_2$, sintering at 70° and melting at 90° has been obtained; it gives the typical catechol reaction. The following constitution is suggested: $C_6H_3(OH)_2\cdot CH(NHMe)\cdot CH_2\cdot OH$ [$CH:(OH)_2 = 1:3:4$]. J. J. S.

Organic Colloids from Town Sewage. WILHELM BILTZ and OTTO KRÖHNKE (*Ber.*, 1904, 37, 1745—1754. Compare Biltz, this vol., ii, 324).—The organic substances in sewage are mostly in solution as colloids. On dialysis, the inorganic constituents rapidly vanish, but about one-half or one-third of the organic constituent cannot be dialysed. On passing an electric current, the amount of oxidisable substance at the anode increases, whilst that at the cathode decreases, showing that the putrefactive matter in sewage is charged negatively relatively to water. This is precipitated by positively charged colloids such as iron or zirconium hydroxides. The authors extend their results to explain the theory of the bacterial method of treating sewage. E. F. A.

Enzyme Actions considered as Equilibria in a Homogeneous System. ARIE W. VISSER (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 605—609).—From his experiments, the author concludes that sucrose may be regenerated to a slight extent from dextrose and lævulose by means of invertase. Further, salicin may be regenerated from saligenin and dextrose by means of emulsin. Invertase and emulsin retain their quantitative activity for some weeks in sterilised solutions. The average factor for the change of velocity of the sucrose decomposition = 2 for 10° between 0° and 25°. By a change of temperature from 0° to 25°, the equilibrium is displaced very little, or not at all. At a definite temperature, the change in concentration of the enzymes has no influence on the equilibrium, but only on the velocity. The intensity of the invertase is smaller in proportion as the quantity of invert sugar present with

the same amount of sucrose is greater. The intensity depends not only on the quantity of invert sugar, but also on the quantity of sucrose present in the solution; it is smaller when this quantity is greater. The reversible enzyme actions observed proceed very slowly.

A. McK.

Influence of Acidity on Enzymes. PAUL PETIT (*Compt. rend.*, 1904, 138, 1003—1004).—It is generally admitted that barley contains an enzyme which saccharifies, but does not liquefy, starch paste, the liquefying action being only developed on germination; the author, however, finds that the same effect is produced by simply varying the acidity. Infusions of barley flour made with distilled water, or with solutions containing 0·2, 0·49, 0·98 grams of lactic acid per litre, were examined in respect of their action on starch paste; the first saccharified, but did not liquefy, the paste; the first two acid solutions both liquefied and saccharified, whilst the third did not liquefy, and only saccharified to a slight extent. Further experiments on the influence of traces of alkali on the action of infusions of barley served to show that the enzyme forms a compound with the alkali which is broken down by acids without the enzyme suffering any change, and the conclusion is drawn that the saccharifying enzyme in barley is in a state of combination which is destroyed by acids, and that a variation in the acidity confers the power of liquefying on the enzyme, independently of germination. M. A. W.

Probable Constitution of the Diastase of Rennet. ALBERTO SCALA (*Chem. Centr.*, 1904, i, 1019; from *Staz. sperim. agrar. ital.*, 36, 941—944).—The author has arrived at the following conclusions: (1) phosphoric acid is not combined with the diastase of rennet in the form of an ester, but is attached to the amino-groups forming a simple salt. (2) The mercury compound is a true substitution product, the mercury taking the place of hydrogen atoms of the amino-groups. (3) The diastase is an albumose. (4) The diastases and their mercury compounds are oxidised by distilled water, drinking-water containing earthy carbonates, and all oxidising agents. By slight oxidation, the lateral amino-groups are split off as ammonia, whilst by the action of potassium permanganate ammonia and nitrous acid are formed. (5) The activity of the diastases depends on the presence of the amino-groups; when all these groups contain mercury, the compound has no longer the power of coagulating milk, but when only a portion of the groups contain mercury, the compound retains this power. (6) Acids and mercury render the diastases less liable to oxidation, although they do not completely prevent it. E. W. W.

Action of Formaldehyde on the Diastatic Force of Malt. KARL J. SOMLÓ and ALADÁR VON LÁSZLÓFFY (*Chem. Centr.*, 1904, i, 1365; from *Oesterr. Chem. Zeit*, 7, 126—128).—Experiments on the action of various antiseptics on green malt have shown that most of these substances have an injurious effect on the diastase. In some cases, however, it has been found possible to prevent this action by modifying the conditions with reference to time and the method of

action. In all cases, it is, of course, necessary to completely wash out the antiseptic before testing the activity of the malt. The action of the diastase of a green malt was found to be considerably increased by treating it with a 2 or 5 per cent. solution of formaldehyde for a time varying from 20 minutes to 4 hours. Immersion of the malt in a 2 per cent. solution of commercial formaldehyde for 2 hours was sufficient to cause a pure fermentation. The hypothesis of the formation of starch from formaldehyde on the green plant possibly finds some confirmation in these facts. E. W. W.

The Function of Peroxides in the Living Cell. VIII. Peroxydases. Alexis Bach and Robert Chodat (*Ber.*, 1904, 37, 1342—1348. Compare Abstr., 1902, ii, 344, 522; 1903, i, 377, 378, 671; this vol., i, 359).—Preparations of peroxydase from horse-radish are free from oxygenase, catalase, amylase, invertase, emulsin, and proteolytic enzymes. The action of peroxydase is more easily studied quantitatively than that of a hydrolytic enzyme, from the fact that the quantities of all the substances taking part in the reaction can be measured. Pyrogallol is not attacked by either hydrogen peroxide or peroxydase separately, and since the product of the reaction, purpurogallin, is insoluble, the reaction proceeds completely in one direction. With constant quantities of hydrogen peroxide and pyrogallol, the purpurogallin formed is proportional to the peroxydase added, and with constant peroxydase and pyrogallol the purpurogallin is proportional to the hydrogen peroxide added. The concentration of the pyrogallol is without influence. Peroxydase thus reacts with hydrogen peroxide in a constant proportion, and must probably be considered as forming a definite compound with it. When equivalent solutions of peroxydase and hydrogen peroxide are mixed, both compounds disappear within 24 hours without evolution of oxygen. C. H. D.

Yeast Catalase. Neumann Wender (*Chem. Zeit.*, 1904, 28, 300—301, 322—323).—Since Omelianski has shown (this vol., ii, 277) that the decomposition of formic acid into hydrogen and carbon dioxide by means of *Bacillus formicicum* is not due to an enzyme, but is occasioned by the living plasma, the author has studied the decomposition of hydrogen peroxide by yeast catalase, and concludes from his experiments that the catalytic decomposition observed is enzymatic. Various specimens of yeast were taken and the amount of oxygen evolved from hydrogen peroxide under the influence of a given weight of yeast in a given time was determined. Dead yeast, prepared by the alcohol-ether method of Albert, or by the acetone method of Rapp, could still induce the catalytic decomposition of hydrogen peroxide.

The influence of temperature on the catalysis was studied. There was no diminution in activity when the yeast was heated for one hour at temperatures ranging from 10° to 50°; at 60°, the yeast lost considerably in activity, and at 70° it lost its power entirely. More exact determinations showed that the temperature at which yeast ceased to be active was 68—72°, and approximated to that at which melibiase and invertase lose their specific properties.

The catalytic action of zymase on hydrogen peroxide was also

examined. Bottom yeast, when kept for some time at 45—50°, lost entirely its power of inducing alcoholic fermentation, but the catalytic action on hydrogen peroxide was quite as marked as it was before the temperature was raised. Further, yeast in which the maltase had been destroyed, still possessed its catalytic power. During the catalysis of hydrogen peroxide by yeast, the zymase in the latter diminishes slightly in activity. The volume of oxygen obtained by the action of yeast on hydrogen peroxide in the presence of definite amounts of acetic, oxalic, tartaric, lactic, sulphuric, and hydrochloric acids, sodium carbonate, sodium hydroxide, silver nitrate, mercuric chloride, alcohol, ether, and potassium thiocyanate respectively was measured. Yeast catalase was shown to be remarkably stable towards the substances just enumerated.

Yeast catalase, in the dry condition, can be heated at 100° without losing its activity. A. McK.

Fermentation Experiments with Extract from Top-fermentation Yeast. ARTHUR HARDEN and WILLIAM JOHN YOUNG (*Ber.*, 1904, 37, 1052—1070).—With sucrose and with dextrose the sugar-fermentation by the extract was practically identical, but in each case was far less than with Buchner's extract from bottom-yeast. The self-fermentation of the extract was very variable, ranging from 0·02 to 0·32 gram of carbon dioxide per 25 c.c. of extract; in absolute measure it corresponds closely with the figures given by Buchner for bottom-yeast (0·10 to 0·459), and by Macfadyen, Morris, and Rowland for top-yeast (0·06 to 0·4959, Abstr., 1901, i, 59). As the fermentation of added sugar proceeds only slowly as compared with that produced by Buchner's extract, the self-fermentation represents a considerable proportion of the total in these cases. It is also noticeable that the fermentation, although much smaller in extent, is proportionately much more rapid than that produced by Buchner's extract; the total fermentation was seldom greater than 1·5 times that in the first 24 hours, whilst Buchner found a ratio ranging from 1·5 to 3·0; this is probably due to the presence of a smaller proportion of xymase or a difference in the proportion of proteolytic enzyme.

No difference was observed in a series of experiments in which kieselguhr was not used in preparing the extract, which was obtained simply by the action of sand.

The fermentation of pure yeast-glycogen by the extract proceeds to a much smaller extent than when an equivalent quantity of dextrose is added to the extract; the yield of carbon dioxide is, however, in all cases considerably greater in presence of glycogen than in the self-fermentation of the simple extract.

Both when the extract is allowed to ferment by itself, and when dextrose is added, the weights of alcohol and carbon dioxide produced are approximately equal, the theoretical ratio is 1·04, and the values found were 0·90, 1·12, 0·95, 0·91, and 0·92; similar results were obtained by Buchner, whilst Macfadyen, Morris, and Rowland obtained similar results only with very energetic fermentation.

Dilution of the extract with water produces no appreciable effect on the self-fermentation, but in presence of dextrose, dilution with

3 volumes of water reduces the yield of carbon dioxide to 0·5 or 0·7 of that with undiluted extract; dilution with sugar-solution, on the other hand, produces little or no effect. This differs from Macfadyen, Morris, and Rowland's results, who concluded that dilution with one or two volumes of water stopped both the self-fermentation and the sugar-fermentation, but agrees with Buchner's results, who did not study the self-fermentation, but found that dilution slightly reduced the sugar-fermentation.

In agreement with the observations both of Macfadyen, Morris, and Rowland, and of Buchner, the weight of sugar removed from the solution was always greater than that calculated from the weight of carbon dioxide and alcohol produced. The sugar appears, however, not to be decomposed, but converted into a form which is not reducible as such, but becomes reducible again when hydrolysed by acids. As dextrose is decomposed by acids, it was necessary to make a correction for this decomposition before trustworthy results could be obtained; the correction was determined by experiments with pure dextrose, and was found to be proportional to the total weight of dextrose, both in $N/2$ and in $3N$-acid solutions. Whether the non-reducible product is of the nature of a carbohydrate could not be determined, as all attempts to isolate it were unsuccessful. It is apparently produced not by xymase, but by some different enzyme, since the weight of sugar changed in this way is very much the same in solutions which undergo a large, and those which undergo only a slight, fermentation.

T. M. L.

Preparation of Organo-lead and Mercury Compounds. Paul Pfeiffer and P. Truskier (*Ber.*, 1904, 37, 1125—1127).—Lead tetraphenyl (compare Polis, Abstr., 1888, 283) is readily obtained by the action of lead chloride on an ethereal solution of magnesium phenyl bromide. Lead triethyl iodide may be obtained from lead chloride and magnesium ethyl iodide. Mercury diphenyl melting at 120° may be obtained by a similar method. J. J. S.

Organic Chemistry.

Electrolytic Preparation of Chloroform from Acetone. JOHN E. TEEPLE (*J. Amer. Chem. Soc.*, 1904, 26, 536—543. Compare this vol., i, 362).—When a solution of sodium or potassium chloride containing acetone is electrolysed, chloroform is produced. Sodium hypochlorite is formed from the action of the chlorine liberated at the anode, on the sodium hydroxide formed at the cathode; the sodium hypochlorite then acts on the acetone. The solution should be only feebly, if at all, alkaline, the temperature is kept below 25°, whilst a high current density is employed at the cathode and a comparatively low one at the anode.

The course of the electrolysis was followed by determining the amount of chloroform produced after definite times and by titrating the alkali produced with trinitrobenzene as indicator; it was shown how the yield of chloroform is diminished if the alkali is allowed to accumulate. A. McK.

Differentiation between Primary, Secondary, and Tertiary Alcohols of the Fatty Series. ANDRÉ KLING and MARCEL VIARD (*Compt. rend.*, 1172—1173).—The method is based on the behaviour of the three classes of alcohols on being heated. At the temperature of boiling naphthalene (218°) tertiary alcohols are dehydrated, whilst primary and secondary derivatives remain intact. At a still higher temperature, the boiling point of anthracene (360°), both tertiary and secondary alcohols are decomposed; the primary compounds alone remain unacted on. To determine whether an alcohol is primary, secondary, or tertiary, it is only necessary to measure the vapour density at 218° and 360°; Victor Meyer's method may be conveniently used. It is shown that the method is applicable to all primary alcohols up to those containing seven carbon atoms, to secondary alcohols as far as derivatives of nine carbon atoms, and to tertiary alcohols with twelve carbon atoms. Aromatic and unsaturated alcohols do not give satisfactory results. S. S.

Alkyloxides. JULIUS W. BRÜHL (*Ber.*, 1904, 37, 2066—2068. Compare Brühl and Biltz, Abstr., 1891, 656).—Metallic sodium is finely divided under boiling xylene (*Ber.*, 1902, 35, 3516), and a further quantity of dry xylene is added so that there are 250 c.c. of liquid for each gram-molecule of sodium. The theoretical amount of methyl alcohol dissolved in twice its volume of dry xylene is run in, whilst the mixture is kept cool and well stirred by aid of the apparatus recently described (this vol., ii, 248). The reaction is completed by gently warming, and should not take more than a few hours. The sodium methoxide obtained as a snow-white, flocculent mass suspended in the xylene, is free from methyl alcohol, and is extremely active. Other alkyloxides may be prepared in a similar manner. Sodium amyloxide is soluble in benzene. J. J. S.

Synthetical *iso*Amyl Alcohol and the Amyl Alcohol of Commerce. René Locquin (*Bull. Soc. chim.*, 1904, [iii], 31, 599—601).—*iso*Amyl alcohol, prepared by Grignard and Tissier's method from *iso*butyl chloride and trioxymethylene, boils at 131° (corr.) under 765 mm. pressure, has a sp. gr. 0·823 at 0°/4°, furnishes an iodide boiling at 147° (corr.) under 765 mm. pressure, and a phenylurethane which melts at 54° (compare Hofmann, *Annalen*, 1850, 74, 16). The iodide prepared from ordinary amyl alcohol boils at 144—150° and the crude phenylurethane from this source melts at 40° and, owing to its ready solubility, is difficult to purify. The author considers that in view of these differences care should be taken, in describing amyl derivatives obtained from ordinary amyl alcohol, to specify the nature of the amyl radicle. T. A. H.

Dichloromethyl Oxide. Marcel Descudé (*Compt rend.*, 1904, 138, 1110—1112. Compare Abstr., 1901, i, 504, 644; 1902, i, 339, 738).—Trioxymethylene reacts with phosphorus trichloride in the presence of a small quantity of fused zinc chloride to form dichloromethyl oxide boiling at 102—105° under the ordinary pressure, and the yield is equal to the weight of trioxymethylene taken. The product of the action of phosphorus trichloride on a 40 per cent. solution of formaldehyde is the same as that obtained by the action of hydrogen chloride on a concentrated solution of formaldehyde (compare Litterscheid, Abstr., 1901, i, 443, and Coops, Abstr., 1902, i, 77); it has the composition $4CH_2O,3HCl$, and the probable constitution is represented by the formula $CH_2{<}\begin{matrix}O{\cdot}CH_2\text{———}OHCl\\OHCl{\cdot}CH_2{\cdot}OHCl\end{matrix}{>}CH_2$.

M. A. W.

Application of the Grignard Reaction to the Halogen Ethers of Tertiary Alcohols. Louis Bouveault (*Compt. rend.*, 1904, 138, 1108—1110).—*tert.*-Amyl and -butyl chlorides form additive compounds with magnesium at temperatures between 5° and 15°; at higher temperatures, a secondary reaction takes place with the formation of the corresponding paraffin and olefine. These magnesium derivatives react normally with carbon dioxide, magnesium *tert.*-butyl chloride giving a yield of 30 per cent. of pivalic acid, and magnesium *tert.*-amyl chloride a yield of 60 per cent. of *aa*-dimethylbutyric acid. Magnesium *tert.*-butyl chloride reacts with methyl formate to form *tert.*-butylcarbinol and a small quantity of the corresponding aldehyde; and with dimethylformamide to yield a small quantity of an aldehyde not yet identified, the semicarbazone of which melts at 192°; magnesium *tert.*-amyl chloride reacts with diethylformamide to give *β*-*iso*amylene (trimethylethylene) and a basic substance, $C_{10}H_{23}N$, probably $CMe_2Et{\cdot}CH_2{\cdot}NEt_2$, boiling at 165—166°, or at 52° under 10 mm. pressure. M. A. W.

***iso*Nitrosoacetic Esters.** Louis Bouveault and André Wahl (*Bull. Soc. chim.*, 1904, [iii], 31, 675—679. Compare Bouveault and Locquin, Abstr., 1902, i, 704 and 705).—When nitrosylsulphuric acid is added to ethyl acetate, a vigorous reaction ensues, which, when

moderated by previous solution of the reacting substances in sulphuric acid and cooling to $-10°$, gives rise to the formation of acetic acid and ethyl *iso*nitrosoacetate, $OH\cdot N:CH\cdot CO_2Et$. The latter crystallises in long, white needles from ether on addition of light petroleum, melts at 35°, and boils at 110—115° under 15 mm. pressure (compare Cramer, Abstr., 1892, i, 699). The free acid crystallises in prisms, melts at 143—144°, and dissolves in aqueous solutions of the alkali hydroxides with a yellow colour. The *methyl* ester, similarly prepared, crystallises in fine prisms, melts at 55°, boils at 100° under 15 mm. pressure, and is very soluble in water; the iso*butyl* ester is a slightly coloured, viscid liquid which distils at 117—118° under 10 mm. pressure, has a sp. gr. 1·082 at 0°/4°, and is insoluble in water, but dissolves in alkaline liquids with a yellow colour.

The authors consider that in the formation of these substances an *iso*nitrosoacetoacetic ester is first formed and that this subsequently undergoes hydrolysis, forming acetic acid and the *iso*nitrosoacetic ester. The fact that ethyl *iso*nitrosoacetoacetate, dissolved in sulphuric acid, can be recovered without the formation of ethyl *iso*nitrosoacetate is, however, not in harmony with this hypothesis. T. A. H.

Action of Nitrogen Trioxide and Peroxide on Nitrosoacetic Esters. Louis Bouveault and André Wahl (*Bull. Soc. chim.*, 1904, [iii], 31, 679—682. Compare Abstr., 1903, i, 677, and preceding abstract).—When ethyl *iso*nitrosoacetate is treated with nitrogen peroxide, there is formed ethyl nitro*iso*nitrosoacetate,

$$OH\cdot N:C(NO_2)\cdot CO_2Et$$

(Jovitschitsch, Abstr., 1898, i, 64, and 1902, i, 202), and, as the result of the partial decomposition of this, ethyl bisanhydronitroacetate, $C_2(NO)_2(CO_2Et)_2$.

When a current of nitrogen trioxide is passed through *iso*butyl *iso*nitrosoacetate, the temperature being maintained below 30—35°, and the resulting *iso*butyl oximinonitroacetate is distilled, a violent decomposition ensues. This may be moderated by previous solution of the reaction product in *iso*butyl alcohol, and when such a solution is distilled iso*butyl glyoxalate* and iso*butyl bisanhydronitroacetate* are produced. The former is a pungent, mobile, yellow liquid, which boils at 75—80° under 15 mm. pressure, readily combines with water, and reduces an ammoniacal solution of silver oxide in the cold; the corresponding *semicarbazone* forms white leaflets and melts at 214—215°. *iso*Butyl bisanhydronitroacetate, $C_2(NO)_2(CO_2\cdot C_4H_9)_2$, is a viscid, yellow liquid which boils at 180—185° under 15 mm. pressure, has sp. gr. 1·156 at 0°/4°, and is insoluble in water.

Corresponding products are obtained when ethyl *iso*nitrosoacetate is similarly treated. T. A. H.

Pentenoic and Hexenoic Acids. Fritz Fichter and Alfred Pfister (*Ber.*, 1904, 37, 1997—2001).—The following improvements have been made in Fittig and Spenzer's method (Abstr., 1895, i, 204) of preparing Δ^{β}-pentenoic acid. Ethyl acetylsuccinate is prepared by means of ethyl bromoacetate, and is reduced by aluminium amalgam to ethyl methylparaconate, which boils at 156° under 17 mm. pressure;

the ester is hydrolysed to its acid by an excess of aqueous barium hydroxide.

Δ^{α}-Hexenoic acid is best prepared by heating ethyl α-bromohexoate with quinoline at 185°; the product is a mixture of ethyl Δ^{α}-hexenoate with a small quantity of the isomeric Δ^{β}-hexenoate and is hydrolysed to the corresponding acids, which are then separated by Fittig's method. Δ^{γ}-Hexenoic acid is oxidised by cold aqueous potassium permanganate to acetic acid and succinic acid.

Δ^{δ}-Hexenoic acid (compare Wallach, Abstr., 1900, i, 590) boils at 203°, has a sp. gr. 0·9639 at 19·2°, n_D 1·4375 at 19·1°, and a mol. refraction 31·02.

The hexenoic acids are best characterised by their *p*-toluidides, which are purified by distillation under reduced pressure.

Δ^{α}-*Penteno*-p-*toluidide* boils at 230—235° under 20 mm. pressure, and crystallises from 50 per cent. acetic acid in long clusters of needles melting at 110°. Δ^{β}-*Penteno*-p-*toluidide* crystallises from hot water in lustrous leaflets and melts at 106°. Δ^{γ}-*Penteno*-p-*toluidide* boils at 205° under 16 mm. pressure, separates from light petroleum in lustrous needles, and melts at 81·5°. The p-*toluidide* from Δ^{α}-hexenoic acid boils at 205—215° under 13 mm. pressure, crystallises from benzene in slender needles, and melts at 125°; that from Δ^{β}-hexenoic acid crystallises from light petroleum in leaflets melting at 95·5°, whilst that derived from Δ^{γ}-hexenoic acid boils at 200—205° under 12 mm. pressure and melts at 103°. Δ^{δ}-*Hexeno*-p-*toluidide* boils at 220° under 14 mm. pressure and crystallises from light petroleum in needles melting at 75°.

o-*Nitro*-Δ^{α}-*hexeno*-p-*toluidide*, prepared by nitrating the *p*-toluidide of Δ^{α}-hexenoic acid, crystallises from alcohol in slender, yellow needles and melts at 87°.

*Phenyl*iso*crotonic anhydride*, $C_{20}H_{18}O_3$, obtained by the action of phosphorus oxychloride on sodium phenyl*iso*crotonate (2 mols.), crystallises from benzene in white leaflets, melts at 120—121°, and combines with aniline to form *phenyl*iso*crotonanilide*, $C_{16}H_{15}ON$, which crystallises from a mixture of benzene and light petroleum in spangles and melts at 89—90°. *Phenyl*iso*crotono*-p-*toluidide* forms white leaflets and melts at 149°. W. A. D.

New Acids of the Oleic Series. I. Δ^{β}-Oleic Acid. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1903—1904, 39, 552—560).—α-*Iodostearic acid*, $CH_3\cdot[CH_2]_{15}\cdot CHI\cdot CO_2H$, prepared by the action of alcoholic potassium iodide on α-bromostearic acid, crystallises from alcohol or light petroleum in shining, white plates melting at 66°; it is stable towards light and dissolves in the ordinary organic solvents.

Δ^{β}-*Oleic acid*, $CH_3\cdot[CH_2]_{14}\cdot CH{:}CH\cdot CO_2H$, obtained, together with α-hydroxystearic acid, by the action of alcoholic potassium hydroxide on α-iodostearic acid, crystallises from alcohol in broad plates or slender, white needles, melts at 59°, and resolidifies at 52°; it is stable in the air and is moderately soluble in light petroleum and extremely so in ether or chloroform; on fusion with potassium hydroxide, it yields palmitic and acetic acids. Its *sodium* salt crystallises from alcohol in prisms soluble in water; the *calcium* salt (with H_2O) dissolves

slightly in alcohol; the *barium* salt is insoluble in water or alcohol, as is also the *silver* salt, which blackens in the light. The *ethyl* ester melts at 15°, distils unchanged at a temperature above 360°, and is miscible with the ordinary organic solvents. The *amide*,

$$CH_3\cdot[CH_2]_{14}\cdot CH\colon CH\cdot CONH_2,$$

crystallises from alcohol in prisms, melts at 107—108°, and dissolves readily in chloroform and, to a slight extent, in acetone or benzene.

βγ-Dibromostearic acid, $CH_3\cdot[CH_2]_{14}\cdot CHBr\cdot CHBr\cdot CO_2H$, prepared by the action of bromine on Δ^{β}-oleic acid, separates from light petroleum in white prisms, melts at 71—72°, and dissolves in the ordinary organic solvents. T. H. P.

Transformation of Sorbic Acid into Amino-acids. EMIL FISCHER and FRITZ SCHLOTTERBECK (*Ber.*, 1904, 37, 2357—2362).—E. Fischer and Roeder have shown (Abstr., 1902, i, 124) that the amino-grouping in the aminobutyric acid, formed from crotonic acid by the action of ammonia, is in the β-position, whilst it has been shown by Wender that β-aminopropionic ethers result from the action of ammonia on esters of acrylic acid. The yield of amino-acid is, however, in such cases slight.

Whilst monoamino-acids can be synthesised by methods more convenient than that of the addition of ammonia to unsaturated acids, diamino-acids, especially those in which the amino-groups are in the 1 : 3- or 1 : 4-positions relatively to one another, are synthesised with more difficulty. The authors have accordingly studied the action of ammonia on sorbic acid, a type of unsaturated acid containing two double linkings, with the view of devising a general method for the syntheses of diamino-acids.

When sorbic acid is heated with an aqueous solution of ammonia at 130°, practically no addition of ammonia takes place; when, however, it is heated with a large excess of an aqueous solution of ammonia, saturated at 0°, for 20 hours at 150°, the main product is a yellow gum, which has a strongly alkaline reaction and is very easily soluble in water and in alcohol. It could not be obtained crystalline, but it shows all the characteristics of a diamino-acid and forms a crystalline *picrate*, $C_6H_{14}O_2N_2,C_6H_3O_7N_3$, which melts at 185·5—186·5° (corr.). The acid in question is regarded as a diaminohexoic acid, but is different from the known αδ-diaminohexoic acid (*i*-lysine). When it is heated for several hours at 150°, ammonia and water are evolved, and a substance is obtained which separates from ether in colourless prisms and melts at 109° (corr.), and is probably *aminohexenoic anhydride*, C_6H_9ON, derived from the unsaturated aminohexenoic acid, $C_6H_{11}O_2N$. The anhydride is easily soluble in water, alcohol, ethyl acetate, benzene, and pyridine, and is fairly stable towards bases; it is not changed when boiled for a short time with aqueous barium hydroxide, but, when heated for several hours with an excess of the latter, it is converted into an amino-acid, which has properties like those of pyrrolidinecarboxylic acid, and is possibly methylpyrrolidinecarboxylic acid.

In the synthetical diaminohexoic acid, obtained in the manner

described, the amino-grouping is considered to be in the γ- or δ-position relatively to the carboxyl grouping.

When β-vinylacrylic acid is heated with ammonia at 150°, it also forms a diamino-acid. A. McK.

Transformations of Salts of Pyruvic Acid. III. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1904, 23, 131—146. Compare Abstr., 1901, i, 130; and 1902, i, 72).—The author has already shown that ammonium pyruvate is converted by pyruvic acid into α-acetylaminopropionic acid, and he now explains this transformation by assuming that the acid first formed, $NH{:}[CMe(OH){\cdot}CO_2H]_2$, becomes converted into the lactone, which loses first a molecule of carbon dioxide and then a molecule of water, forming α-acetylaminopropionic acid.

When a solution of pyruvic acid in water is neutralised with ammonium carbonate, the liquid after four days gives with phenylhydrazine a mixture of the phenylhydrazones of pyruvic and α-keto-γ-aminobutane-$\alpha\gamma$-dicarboxylic acids. Eventually it becomes brown and deposits crystals of the ammonium salt of 2-methylpyridine-4 : 6-dicarboxylic acid. The latter, when prepared from the recrystallised sodium salt, is white and melts at 274° (compare Altar, Abstr., 1887, 378). When solutions of molecular quantities of pyruvic acid and ammonia in dilute alcohol are mixed, the resulting liquid becomes warm and deposits a white precipitate. A similar product is also formed when ammonia is used in excess. These precipitates give with phenylhydrazine a mixture of the phenylhydrazones of pyruvic and α-keto-γ-aminobutane-$\alpha\gamma$-dicarboxylic acids, and the proportion of the phenylhydrazone of pyruvic acid formed is augmented if the precipitates are first boiled either with water or with dilute solution of ammonia. A tabular statement of the proportions of the two acids in these precipitates prepared under various conditions is given in the original. These products contain no metapyruvic or parapyruvic acids.

α-Keto-γ-aminobutane-$\alpha\gamma$-dicarboxylic acid phenylhydrazone may be separated from the phenylhydrazone of pyruvic acid by washing with water and alcohol and recrystallising from boiling water. It forms spheroids of needles and melts and decomposes at 156°, is readily soluble in acids and alkalis, but only slightly so in ether, alcohol, and cold water. When the phenylhydrazone is warmed with hydrochloric acid of sp. gr. 1·14, it is converted into 3-keto-2-phenyl-4-methyl-2 : 3-dihydro-1 : 2-diazine-6-carboxylic acid (Abstr., 1902, i, 122). T. A. H.

Action of Hydrochloric Acid on Pyruvic Acid. IV. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1904, 23, 147—154. Compare Abstr., 1901, i, 446; 1902, i, 122; 1903, i, 146).—When β-bromo-α-keto-Δ^{β}-butene-$\alpha\gamma$-dicarboxylic acid is boiled under a reflux condenser with hydrochloric or sulphuric acid, carbon dioxide is evolved and an acid which may have the formula

$$CHO{\cdot}CBr{:}CMe{\cdot}CO_2H \text{ or } CHMe{:}CBr{\cdot}CO{\cdot}CO_2H$$

is formed; this melts at 95° and is readily soluble in alcohol, ether, and chloroform. When β-bromo-α-keto-Δ^{β}-butene-$\alpha\gamma$-dicarboxylic acid

is dissolved in acetic anhydride and the solution is evaporated under reduced pressure over sulphuric acid, a *mixed anhydride* of acetic acid and the $\alpha\gamma$-lactone of β-bromo-α-keto-γ-hydroxybutane-$\alpha\gamma$-dicarboxylic acid, $CO<\substack{CHBr \\ CO-O}>CMe\cdot CO\cdot OAc$, is formed; this is crystalline and melts at 86°. A similar *product*, $OAc\cdot CO\cdot CMe\!:\!CBr\cdot CO\cdot CO_2Et$, is formed by the action of acetic anhydride on the monoethyl ester; this is an oil readily resolved by water into its generators. The formation of these anhydrides indicates that in the production of β-bromo-α-keto-Δ^{β}-butene-$\alpha\gamma$-dicarboxylic acid by the action of bromine on the $\alpha\gamma$-lactone of α-keto-γ-hydroxybutane-$\alpha\gamma$-dicarboxylic acid, the lactone ring is not broken by the introduction of the bromine atom, but by the action of the hydrogen bromide simultaneously formed.

Ethyl α-keto-Δ^{β}-butene-$\alpha\gamma$-dicarboxylate, $CO_2Et\cdot CMe\!:\!CH\cdot CO\cdot CO_2Et$, prepared by the action of hydrogen chloride on a solution of the lactone in alcohol, boils at 182—184° under 28 mm. pressure (compare Genvresse, Abstr., 1893, i, 552) and furnishes an oily *phenylhydrazone.*

The substance, $C_{12}H_{10}O_3N_2$, obtained by the action of hydrochloric acid on the phenylhydrazone of the $\alpha\gamma$-lactone of α-keto-γ-hydroxy-butane-$\alpha\gamma$-dicarboxylic acid (Abstr., 1902, i, 122) gives with acetic anhydride an *acetyl* derivative which crystallises in colourless needles, melts and decomposes at 264°, and dissolves both in alcohol and in aqueous solution of sodium hydroxide with a yellow colour. From the substance, $C_{12}H_9O_4N,H_2O$, prepared from the foregoing compound by the action of sodium hydroxide, a *nitro*-derivative melting at 218° has been obtained. T. A. H.

Preparation of Substituted Acylacetic Esters. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 588—593. Compare Abstr., 1901, i, 311; 1902, i, 704; and 1903, i, 63 and 142).—Further details are given regarding the preparation of substituted acylacetic esters by the simultaneous action of alkyl haloids and sodium alkyloxides on the *C*-esters of the acylacetoacetates already described by the author (Abstr., 1902, i, 704). With primary alkyl iodides, a yield of 70—75 per cent. is obtained, and with the secondary iodides only 25—35 per cent., due to the formation of hydrogen iodide from these, which liberates the ester from its alkaline solution, and this is then hydrolysed forming either acetoacetic ester or an unsubstituted acylacetic ester. The alkyl bromides give smaller yields than the iodides.

The sodium alkyloxide (1 mol.) is dissolved in the ester, and after twelve hours the alkyl iodide is added and the mixture heated in closed vessels at 100—110° for at least six hours; the alcohol is distilled off and the residue washed with sodium carbonate and thio-sulphate and extracted with ether. The oil left on distilling off the ether is fractionated, the last fraction containing the required product.

The substituted acyl esters are colourless, mobile liquids; they give violet colorations with ferric salts, are insoluble in aqueous alkaline solutions, and show all the properties of β-ketonic esters. When dissolved in alcohol and heated for one hour at 100° with a slight

excess of hydrazine hydrate, they furnish disubstituted pyrazolones. The latter formed from complex esters are liquid, but distil with slight decomposition under reduced pressure; the others crystallise readily from boiling benzene or dilute alcohol and decompose slowly unless kept in closed vessels. T. A. H.

Homologues of Butyrylacetic and *iso*Valerylacetic Esters. René Locquin (*Bull. Soc. chim.*, 1904, [iii], 31, 593—595. Compare Abstr., 1902, i, 704; 1903, i, 143 and preceding abstract).—The following esters were prepared by the general method described in the preceding abstract. Ethyl ethylbutyrylacetate, $CPr^{\alpha}O\cdot CHEt\cdot CO_2Et$, obtained together with some ethyl ethylacetoacetate by the action of ethyl iodide and sodium ethoxide on ethyl *C*-butyrylacetoacetate, boils at 105—108° under 13 mm. pressure and has a sp. gr. 0·975 at 0°/4° (compare Hamonet, Abstr., 1890, 235). When treated with hydrazine hydrate (compare Abstr., 1902, i, 704), it furnishes 4-ethyl-3-propylpyrazolone, which forms brilliant spangles, melts at 165—166° (corr.), and is soluble in ether, slightly so in water and benzene. From the small quantity of ethyl ethylacetoacetate present in the ester employed there was also formed in this reaction some 3-*methyl*-4-*ethylpyrazolone*, which crystallises in brilliant spangles and melts at 195—196° (corr.). *Ethyl propylbutyrylacetate*, $CPr^{\alpha}O\cdot CHPr^{\alpha}\cdot CO_2Et$, boils at 112—113° under 10 mm. pressure and has a sp. gr. 0·958 at 0°/4°. With hydrazine hydrate, it furnishes 3 : 4-*dipropyl*-5-*pyrazolone* which distils at 190—200° under 14 mm. pressure and gradually solidifies.

Ethyl iso*propylbutyrylacetate*, $CPr^{\alpha}O\cdot CHPr^{\beta}\cdot CO_2Et$, is produced only in small quantities by the general reaction; it boils at 111° under 14 mm. pressure, has sp. gr. 0·962 at 0°/4°, and with hydrazine hydrate furnishes 3-*propyl*-4-iso*propyl*-5-*pyrazolone*, which, in the slightly impure form in which it was obtained, melts at 133° (corr.).

*Ethyl ethyl*iso*valerylacetate*, $C_4H_9\cdot CO\cdot CHEt\cdot CO_2Et$, obtained from ethyl iodide and ethyl *C*-*iso*valerylacetoacetate (boiling point 122° under 12 mm. pressure. Compare Bouveault and Bongert, Abstr., 1903, i, 63), boils at 107—108° under 11 mm. pressure, has a sp. gr. 0·959 at 0°/4°, and furnishes with hydrazine hydrate 3-iso*butyl*-4-*ethyl*-5-*pyrazolone*, which forms slender needles, melts at 106° (corr.), and is soluble in ether. T. A. H.

Homologues of Hexoylacetic and *iso*Hexoylacetic Esters. René Locquin (*Bull. Soc. chim.*, 1904, [iii], 31, 595—599. Compare Abstr., 1902, i, 704 and two preceding abstracts).—*Ethyl methylhexoylacetate*, $C_5H_{11}\cdot CO\cdot CHMe\cdot CO_2Et$, obtained by the general method from ethyl *C*-hexoylacetoacetate (*loc. cit.*), boils at 128—129° under 12 mm. pressure, has a sp. gr. 0·963 at 0°/4°, and with hydrazine hydrate furnishes 4-*methyl*-3-*amylpyrazolone*, which crystallises from boiling benzene in brilliant lamellæ and melts at 164—165° (corr.).

Ethyl sec-octylhexoylacetate, of which a yield of 27—30 per cent. was obtained, boils at 183—184° under 11 mm. pressure and has a sp. gr. 0·925 at 0°/4°. There are produced with this ester octylene, octyl alcohol, methyl amyl ketone, ethyl hexoate, ethyl octylacetoacetate, and ethyl hexoylacetate. The last-mentioned ester boils at 116—117°

under 20 mm. pressure and with hydrazine hydrate furnishes 3-amylpyrazolone (compare Bouveault and Bongert, Abstr., 1903, i, 143). On hydrolysis, it gives the corresponding solid *acid*, which crystallises from warm light petroleum in spangles and melts at 73—74°, decomposing at the same time into carbon dioxide and methyl amyl ketone.

Ethyl C-iso*hexoylacetoacetate*, $C_5H_{11}\cdot CO\cdot CHAc\cdot CO_2Et$, prepared by Bouveault and Bongert's process (Abstr., 1903, i, 63), using a chloride (designated natural *iso*hexoyl chloride) obtained from ordinary amyl alcohol, boils at 133—134° under 13 mm. pressure and has a sp. gr. 1·032 at 0°/4°. With methyl iodide it furnishes the corresponding *ethyl methyl*iso*hexoylacetate*, which boils at 117—118° under 13 mm. pressure, has a sp. gr. 0·961 at 0°/4°, and furnishes a corresponding 4-*methyl*-3-iso*amylpyrazolone;* this crystallises in brilliant lamellæ from ether or benzene and in spangles from dilute alcohol and melts at 177—178° (corr.). T. A. H.

Preparation of the Externally- and Internally-compensated Inactive Forms of 2:5-Dihydroxyadipic Acid. E. Rosenlew (*Ber.*, 1904, **37**, 2090—2092).—Two 2:5-dibromoadipic acids were prepared from adipic acid. One of these, designated as the *A* form, separates from formic acid in rosettes of compact leaflets and melts at 191°; it is insoluble in cold water and in boiling benzene, but is readily soluble in ether and in ethyl acetate; the *B* variety separates from formic acid in tiny crystals and melts at 138—139°; it is insoluble in benzene and light petroleum, but is readily soluble in water, ether, and ethyl acetate. By the action of baryta water, the hydroxy-acids corresponding with these dibromo-acids were prepared. *A-2:5-Dihydroxyadipic acid* separates from water in compact, transparent crystals and melts at 173°. *B-2:5-Dihydroxyadipic acid* separates from water in indistinctly crystalline forms and melts at 132—134°. Both acids are sparingly soluble in most organic solvents; the *A*-acid is more readily soluble in water than the *B*-acid. The *A*-acid is probably the externally-compensated, and the *B*-acid the internally-compensated form. A. McK.

Transformation of Unsaturated Acids. Rudolf Fittig (*Annalen*, 1904, **331**, 88—150. Compare Abstr., 1899, i, 332, 333, 417; and this vol., i, 418).—The oxidation of itaconic, aticonic, and mesaconic acids and their derivatives has been studied with the object of confirming the constitution assigned to these substances in previous communications (*loc. cit.*).

Oxidation of Dimethylitaconic and Dimethylaticonic Acids.—[With August Schwärtzlin.]—Dimethylitaconic acid (teraconic acid),

$$CMe_2{:}C(CO_2H)\cdot CH_2\cdot CO_2H,$$

in the form of the sodium salt, was oxidised in dilute (1 per cent.) aqueous solution with 2 per cent. permanganate, the temperature not being allowed to rise above 2°. Acetone was isolated from the products of oxidation by fractionation of the alkaline liquid; acetic acid was the only volatile acid, and oxalic acid was found together with unchanged teraconic acid in the residue from the distillation.

Oxalacetic acid, which Fenton and Jones (Trans., 1900, 77, 77) had found to be very stable, was isolated from the products of oxidation, when the resulting alkaline liquor, the volume of which was kept small, was acidified, extracted with ether to remove unchanged teraconic acid, and then made strongly acid with sulphuric acid and again extracted with ether. It is thus shown that acetone and oxalacetic acid are the primary products of oxidation, and that the latter either breaks up, when heated in alkaline solution, into acetic acid and oxalic acid, or that it is partly further oxidised to malonic acid, which in its turn is oxidised to oxalic acid.

Dimethylaticonic acid, $CH_2{:}CMe{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, was oxidised in the same manner as the last-mentioned acid; an odour of formaldehyde became at once perceptible, and the aldehyde was isolated by cautious distillation. Part of the liquid product of the oxidation was freed from acids by neutralisation with calcium carbonate, and then treated with ammonia and evaporated to dryness, the residue being extracted with ether, when hexamethylenetetramine was obtained, a fact which demonstrated the presence of formaldehyde in the original product. The remainder of the aqueous solution of the oxidation products was extracted first with ether and then with chloroform. From the latter solvent, *iso*heptodilactone (m. p. 116°) was obtained; it is doubtless produced from the dihydroxy-acid,

$$OH{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H,$$

first formed, which is unstable in acid solution. The ethereal extract contained besides a small quantity of unchanged acid also small amounts of acetic acid, the only volatile acid, and lævulic acid (m. p. 32°), which was recognised by conversion into the silver and calcium salts. Formaldehyde and lævulic acid are the main products of the oxidation.

Oxidation of Hexylitaconic and Hexylaticonic Acids.—[With Johann Simon.]—From the oxidation products of hexylitaconic acid, a small quantity of heptaldehyde was isolated by distillation in steam. The mother liquor was acidified with hydrochloric acid and extracted with ether several times. The first ethereal extracts contained unchanged hexylitaconic acid (m. p. 131°); the later extracts contained oxalic acid and *hexylhydroxyparaconic acid*, $\begin{array}{l}CH_3{\cdot}[CH_2]_5{\cdot}CH{\cdot}C(OH)(CO_2H){\cdot}CH_2\\ \qquad\qquad\quad\; | \qquad\qquad\qquad\qquad\quad\;\; | \\ \qquad\qquad\quad\; O\text{———————————}CO\end{array}$,

which were separated by means of their calcium salts. The paraconic acid crystallises from ether in large plates belonging to the rhombic system [$a:b:c = 0{\cdot}82241:1:1{\cdot}48675$], and melting at 103—104°; the *barium* salt crystallises with H_2O, the *calcium* salt with $2\frac{1}{2}H_2O$, and the *silver* salt is anhydrous and amorphous.

When the salts of the paraconic acid are heated with excess of a solution of the alkali hydroxide, they are converted into the salts of *hexylitatartaric* acid; the *barium* salt, $C_{11}H_{18}O_6Ba$, is insoluble and amorphous, the *calcium* salt is similar. On setting free the acid from these salts, hexylitaconic acid was formed.

Hexylaticonic acid, which has been prepared from the hexylitaconic acid in a simpler manner than heretofore, was oxidised in the usual manner and yielded no aldehyde; the acidified liquor was extracted with ether; the unchanged hexylaticonic acid was removed as the

insoluble barium salt, and a new *acid*, $C_{11}H_{18}O_5$, isolated in the form of a soluble barium salt. This acid crystallises from ether and petroleum in needles melting at 126—127°, is dibasic, and, since it neither reacts with phenylhydrazine nor yields a lactone, appears to be the internal anhydride, $\begin{matrix}C_5H_{11}\cdot CH \\ O\text{—}\end{matrix}\!>\!CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, of a dihydroxy-acid; the *barium*, *calcium*, and *silver* salts are amorphous, anhydrous soluble powders. In the mother liquors from which the dibasic acid was separated, a *dilactone*, $C_{11}H_{18}O_4$, was found; it crystallises in needles melting and decomposing at 185—186°.

Oxidation of Methyl- and Ethyl-mesaconic Acids.—[With WILHELM DANNENBERG.]—When methylmesaconic acid,

$$CH_2Me\cdot C(CO_2H):CH\cdot CO_2H,$$

is oxidised, methylpyruvic acid can readily be isolated by distilling in steam and converting the volatile acids into barium salts; its *phenylhydrazone* crystallises in pale yellow needles melting at 144—145°. Formic acid is also found in the distillate, and oxalic and malonic acids in the residue.

On oxidising ethylmesaconic acid and distilling the liquid in steam, formic and butyric acids can be isolated from the distillate in the form of calcium salts. The distillate also contains ethylpyruvic acid, which is purified by distilling the anhydrous mixture of acids obtained from the barium salts. The *barium* salt crystallises with H_2O in sparingly soluble, lustrous leaflets, the *calcium* salts with H_2O in small plates; the *silver* salt forms colourless needles; the *phenylhydrazone* crystallised in pale yellow needles melting and decomposing at 114—115°. The constitution of the ethylpyruvic acid was confirmed by reduction to α-hydroxyvaleric acid.

Action of Bromine on Methylaticonic and iso*Butylitaconic Acids.*—[With OSCAR SHEEN.]—Methylitaconic acid is brominated by adding bromine to an aqueous suspension of the acid in ice-cold water; *methylitaconic acid dibromide*, $CHMeBr\cdot CBr(CO_2H)\cdot CH_2\cdot CO_2H$, separates, whilst bromomethylparaconic acid remains in solution and can be isolated by extracting with ether, and crystallising the residue from the ether, from chloroform. The dibromide melts and decomposes at 178°, and, when warmed with water, is decomposed, yielding *methylaconic acid* and *bromo-Δ^β-pentenoic acid*, $CHMe:CBr\cdot CH_2\cdot CO_2H$, which is separated from the methylaconic acid by its greater solubility in a mixture of chloroform and petroleum; the latter acid crystallises in lustrous plates melting at 54°, and was proved to have the foregoing constitution by reducing it to Δ^β-pentenoic acid by means of sodium amalgam; further, the pentenoic acid on bromination yields $\beta\gamma$-dibromovaleric acid (m. p. 65—65·5°).

Bromomethylparaconic acid, $O\!<\!\begin{matrix}CHMe\cdot CH \\ CO\text{——}CH_2\end{matrix}\!>\!CBr\cdot CO_2H$, forms only a small part of the product of bromination of methylitaconic acid, and crystallises in cubes melting and decomposing at 138°; on reduction, it is converted into methylparaconic acid. On boiling bromomethylparaconic acid with water, *methylaconic acid*, $O\!<\!\begin{matrix}CHMe \\ CO\cdot CH\end{matrix}\!\geqslant\!C\cdot CO_2H$, is formed; it crystallises in small prisms melting at 159·5—160°; its

barium salt forms anhydrous needles and the *calcium* salt is amorphous. On reduction with sodium amalgam, it is converted into methylparaconic acid.

[With JACOB KRAENCKER.]—*iso*Butylitaconic acid, when brominated in the same manner as the methylitaconic acid, yields mainly a dibromide, $C_4H_9\cdot CHBr\cdot CBr(CO_2H)\cdot CH_2\cdot CO_2H$, and *bromo*iso*butylparaconic acid*, $O<\begin{matrix}CH(C_4H_9)\\CO—CH_2\end{matrix}>CBr\cdot CO_2H$. These are separated by adding chloroform to the ethereal solution, when the dibromide separates first; it forms crystalline aggregates melting and decomposing at 168—171°; when boiled with water, it is decomposed yielding *bromo*iso*octenoic acid*, *iso*butylaconic acid (m. p. 170°), which forms the main solid constituent of the mixture, and *iso*butylparaconic acid. *Bromo*iso*butylparaconic acid* crystallises in needles melting and decomposing at 144—145°. *Bromo*iso*octenoic acid*,

$$CH_2Pr^{\beta}\cdot CH:CBr\cdot CH_2\cdot CO_2H,$$

which forms the main product of the decomposition of the dibromo-acid with water, and is separated from the two solid products of the reaction, *iso*butylaconic and *iso*butylparaconic acids, by extraction with petroleum, is purified by distillation in steam, and forms white crystals melting at 14—15°. On reduction with sodium amalgam, it was converted into *iso*octenoic acid (b. p. 231—232°), which was then transformed into *iso*octolactone. K. J. P. O.

A Crystalline Chromous Tartrate. GEORGES BAUGÉ (*Compt. rend.*, 1904, 138, 1217—1220).—The author has obtained an anhydrous, blue, crystalline chromous tartrate, $CrC_4H_4O_6$, by the action of tartaric acid on moist chromous acetate (compare Moissan, Abstr., 1881, 684, 685; 1883, 22). As the salt is readily oxidised, a special apparatus, not yet described, was used, whereby the whole operation, including the filtering and washing, was performed in an atmosphere of carbon dioxide. The salt has a sp. gr. of 2·33 at 15°, is insoluble in cold or boiling water, or water saturated with carbon dioxide, is not acted on by dry chlorine in the cold, but decomposed into chromium sesquioxide and carbon at a slightly higher temperature; is attacked by hydrogen sulphide at a red heat with the formation of a black sulphide and liberation of hydrogen, and is decomposed with the formation of the sesquioxide by the action of dry hydrogen, hydrogen chloride, sulphur dioxide, ammonia, or carbon dioxide at a red heat. Chromous tartrate readily reduces an ammoniacal solution of silver nitrate in the cold, whilst the neutral nitrate is decomposed but slowly. Concentrated solutions of alkali carbonates decompose the tartrate in the cold, forming double carbonates of chromous oxide; if, however, dilute solutions of the carbonates are employed in large excess, the chromous salt is converted quantitatively into chromic oxide (compare Abstr., 1900, ii, 349). M. A. W.

Preparation of $\alpha\beta$-Diketonic Esters. LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1904, 138, 1221—1223).—The method of preparing a ketonic ester by the action of nitrogen peroxide on the corresponding *iso*nitroso-compound, as used in the case of the *iso*-

nitrosomalonic esters (compare Abstr., 1903, i, 677), appears to be of general application. *Ethyl diketobutyrate*, $COMe\cdot CO\cdot CO_2Et$, prepared by the action of nitrous gases on a solution of ethyl *iso*nitrosoacetoacetate in acetic anhydride, is a mobile, orange-yellow liquid boiling at 70° under 13 mm. pressure, possessing the ethereal odour characteristic of diketones, and reacting energetically with water to form a colourless crystalline *hydrate*, $COMe\cdot CO\cdot CO_2Et,\frac{1}{2}H_2O$, which crystallises from anhydrous ether in beautiful, white needles melting at 120°, and is probably identical with the compound obtained by Sachs and Wolff (compare Abstr., 1903, i, 793) by saponifying the condensation product of nitrosodimethylaniline and ethyl acetoacetate. *Ethyl diketobutyrate phenylhydrazone* crystallises in clear yellow prisms melting at 102—103°.

iso*Butyl diketobutyrate*, prepared similarly to the ethyl compound, is an orange-yellow liquid boiling at 96—100° under 18 mm. pressure; it forms a colourless, crystalline *hydrate*, $C_8H_{12}O_4,\frac{1}{2}H_2O$, melting at 96°, a *disemicarbazone* in the form of a white, crystalline powder melting at 254—255° and almost insoluble in the ordinary solvents, and a *phenylhydrazone* crystallising in yellow, rhombohedral plates, melting at 98—99°. M. A. W.

New Polymerides of Formaldehyde. ALPHONSE SEYEWETZ and GIBELLO (*Compt. rend.*, 1904, 138, 1225—1227).—By the action of heat on a mixture of trioxymethylene and water, the author has obtained four polymerides of formaldehyde, which differ in solubilities and melting points from paraformaldehyde, its hydrate, α-trioxymethylene, or ordinary trioxymethylene. The new polymerides are separated by fractional distillation: the first forms a crystalline sublimate in the reflux apparatus, melts at 123°, is soluble in cold water, slightly soluble in boiling alcohol, almost insoluble in ether, and five times as soluble as ordinary trioxymethylene in sodium sulphite solution; the second separates in white flakes from the aqueous distillate, melts at 96—97°, is soluble in cold water, slightly soluble in boiling alcohol, insoluble in ether, and equally soluble as the preceding compound in sodium sulphite solution; the third is extracted by ether from the aqueous mother liquors from which the second is deposited; it melts at 69°, is soluble in water, fairly so in alcohol, and with the exception of α-trioxymethylene (m. p. 60—61°) is the only polymeride of formaldehyde that is soluble in ether; the fourth polymeride separates as white crystals from the liquid left in the flask after the distillation, melts at 92—93°, is soluble in cold water or boiling alcohol, and insoluble in ether; on being heated, it partly sublimes unchanged, and is partly converted into the trioxymethylene melting at 170—171°. Attempts to discover the molecular complexity of these new compounds by molecular weight determinations were unsuccessful; the vapour density method gave in all cases numbers approximating to 30, whilst the cryoscopic method with freshly prepared solutions gave the number 60. M. A. W.

Action of Phosphorus Pentachloride on Chloral. F. GIOLITTI (*Gazzetta*, 1904, 34, i, 247—253).—The action of phosphorus penta-

chloride on chloral yields (1) a *compound*, $CCl_3\cdot CH<^{O}_{O}>PCl_3$, which is an oily liquid having a pungent odour, fuming in the air, and boiling at 238—242°; it has the normal molecular weight in freezing benzene and the normal vapour density under diminished pressure; salts of silver precipitate half the chlorine it contains; (2) a small quantity of tetrachloroethylene. T. H. P.

The Alkyl Allyl and Propenyl Ketones. EDMOND E. BLAISE (*Compt. rend.*, 1904, 138, 1106—1108. Compare this vol., i, 290, 370). —Owing to the greater readiness with which the ethylenic linking in the $\alpha\beta$-position becomes saturated than the same linking in the $\beta\gamma$-position, the alkyl allyl ketones ($CH_2{:}CH\cdot CH_2\cdot COR$) and the isomeric alkyl propenyl ketones ($CH_3\cdot CH_2{:}CH\cdot COR$) behave differently towards such reagents as hydroxylamine and semicarbazide; the alkyl allyl ketones yield the normal oxime and semicarbazone respectively, whilst the alkyl propenyl ketones give with hydroxylamine oximes isomeric with the alkyl allyl oximes, and also soluble hydroxylamino-oximes yielding dibenzoyl derivatives, and with semicarbazide semicarbazido-semicarbazones (compare Power and Lees, Trans., 1904, 85, 635).

The dibromo-derivatives formed by the action of bromine on the two types of unsaturated ketones are unstable liquids that cannot be distilled; on treatment with a solution of an alkali carbonate, the brominated alkyl allyl ketones yield a colourless distillate, whilst brominated alkyl propenyl ketone gives an α-diketone which is readily characterised by its intense greenish-yellow colour and the formation of an osazone. M. A. W.

Starch Conversion in the Mash Tun. ARTHUR R. LING (*J. Fed. Inst. Brewing*, 1903, 9, 446—461).—As the compounds known as malto-dextrins are simply carbohydrates of less complexity than those to which the name dextrin has been applied, the author suggests that the term malto-dextrin be adopted for the whole class of diastatic products, since it indicates their origin and avoids confusion with the dextrin of torrefaction.

Brown, Morris, and Millar have stated that the malto-dextrin obtained by them, which is identical with the malto-dextrin α of Ling and Baker (Trans., 1897, 71, 514), is completely converted into maltose by the action of diastase, but the author finds that this compound (having the constants $[\alpha]_{D3\cdot93}$, 180·5° and $R_{3\cdot93}$, 36·7) yields a mixture containing approximately 90 per cent. of maltose and 10 of dextrose when subjected to the action of active diastase prepared from a low-dried malt for 140 hours at 131° F. The maximum proportion of dextrose appears never to exceed 12 per cent. of the total products, and when this maximum has been reached, further heating at 131° with the enzyme produces a diminution in the amount of this sugar.

Dextrose is formed when starch paste is treated for a long time with diastase solution, but only when the latter has been previously heated to above 140° F. When, however, the products of the partial hydrolysis of starch by diastase unrestricted by heat are isolated and

submitted to the further action of the enzyme, dextrose is always obtained.

The diminution in the amount of dextrose occurring on prolonged action of diastase is attributed to the synthetic action of the enzyme. Dextrose itself, however, could not be made to undergo this condensation change. Lintner's *iso*maltose may possibly be a reversion product of dextrose.

Mashes made with malt starch and with barley starch of various origins, at temperatures below that at which the starch employed gelatinises, show that the changes taking place are considerably different from starch paste conversions, and the results make it probable that the starch undergoes hydrolysis without preliminary gelatinisation. T. H. P.

Analogy between Organic Oxygen and Nitrogen Compounds. W. TSCHELINZEFF (*Ber.*, 1904, 37, 2081—2085).—The author compares different groups of oxygen and nitrogen derivatives as regards their reactions with organo-magnesium compounds, for example, water with ammonia, alcohols with amines (primary and secondary), carbon dioxide with carbylamines, ketones with nitriles, acids with amides, and esters of formic acid with alkylated formamides.

The analogy extends even further, for dimethylaniline can take the place of ether as a solvent in the preparation of Grignard's compounds. J. J. S.

Electrolysis of Tetraethylammonium Iodide. EMIL GOECKE (*Zeit. Elektrochem.*, 1904, 10, 249).—When a solution of tetraethylammonium iodide is electrolysed with platinum electrodes, the main product is tetraethylammonium tri-iodide, NEt_4I,I_2. Small quantities of iodoform are also produced. T. E.

Action of Chloro-formdiethylamide on Alcohols and Phenols. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1904, [iii], 31, 689—691).—Chloro-formdiethylamide, prepared by Michler and Escherich's method (Abstr., 1879, 934), reacts with alcohols and phenols to produce a series of compounds of the type $RO\cdot CO\cdot NEt_2$. With ethyl alcohol, *ethyl diethylcarbamate*, $EtO\cdot CO\cdot NEt_2$, a liquid boiling at 169—172°, is formed; with diethylcarbinol, the *product*, $C_5H_{11}O\cdot CO\cdot NEt_2$, a liquid boiling at 206—208°, is formed, and from symmetrical dichlorohydrin the *substance*, $C_3H_5Cl_2O\cdot CO\cdot NEt_2$, which boils at 259—261° and is insoluble in water, is obtained; and with the diethyl ether of glycerol the *substance*,

$$CH(CH_2\cdot OEt)_2\cdot O\cdot CO\cdot NEt_2,$$

is produced; it is insoluble in water and boils at 260—262°.

Phenyl diethylcarbamate, $PhO\cdot CO\cdot NEt_2$, similarly prepared from phenol, is a viscous liquid which boils at 270—271° and is insoluble in water. From resorcinol, the *substance*, $C_6H_4(O\cdot CO\cdot NEt_2)_2$, a viscous liquid, insoluble in water and boiling at 263—267°, is obtained, and with guaiacol the *product*, $OMe\cdot C_6H_4\cdot O\cdot CO\cdot NEt_2$, which boils at 299—300° and otherwise resembles the foregoing compounds, is procured. T. A. H.

A Naturally-occurring Isomeride of Leucine. I. FELIX EHRLICH (*Ber.*, 1904, 37, 1809—1840. Compare Abstr., 1903, i, 796).—The preparation of *d-iso*leucine from beet sugar is fully described. From the liquors to which the strontia desaccharification process has been applied, a mixture of *r*-leucine, *l*-leucine, and *d-iso*leucine was obtained, from which the latter may be isolated by aid of its copper derivative, which differs from the copper salt of leucine in its great solubility in methyl alcohol.

d-iso*Leucine hydrochloride* forms stellate needles. The *copper* salt of *d-iso*leucine separates in leaflets, grouped in rosettes; it is very readily soluble in benzyl alcohol, ethyl acetoacetate, or benzaldehyde. When heated at 180° with baryta solution, *d-iso*leucine is completely racemised. The copper salt of *r-iso*leucine is also readily soluble in methyl alcohol. The benzoyl, benzenesulphonic, phenylcarbimide, and hydantoin compounds of *d-iso*leucine were prepared by the methods used by E. Fischer for the corresponding derivatives of *l*-, *d*-, and *r*-leucines respectively, and are well adapted for the characterisation of *d-iso*leucine. The *phenylhydantoin* derivative, prepared by the action of hydrochloric acid on the phenylcarbimide, separates from light petroleum in silky needles and melts at 78—79°. As distinct from other derivatives of *d-iso*leucine, it is lævorotatory.

d-*iso*Leucine was also isolated from the products of the action of pancreatic juice on blood fibrin. It has also been isolated as a product resulting from the hydrolysis of ovalbumin by sulphuric acid, from the crude leucine obtained by the putrefaction of beef, and from other sources. The conclusion is drawn that *d-iso*leucine almost invariably occurs along with *l*-leucine as a primary product of proteid hydrolysis.

*d-iso*Leucine is not identical with *d*-α-aminc-*n*-hexoic acid.

The reason why previous investigators have found the isolation of *l*-leucine so difficult is that *d-iso*leucine is also present, and the two isomerides form mixed crystals. About equal parts of *d-iso*leucine and partially racemised *l*-leucine are present in the liquors, to which the strontia desaccharification process has been applied. A. McK.

Betaines. III. δ-Trimethylvalerobetaine. RICHARD WILLSTÄTTER and WALTER KAHN (*Ber.*, 1904, 37, 1853—1858. Compare Abstr., 1902, i, 266; this vol., i, 235).—Although, when heated, α-betaines undergo rearrangement into isomeric esters of tertiary amino-acids, β- and γ-betaines split off trimethylamine. The simplest type of δ-betaine, that derived from trimethylaminovaleric acid, has now been studied.

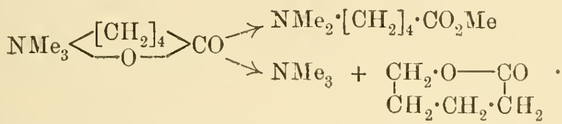
Ethyl δ-trimethylaminopropylmalonate hydrobromide,

$$NMe_3Br\cdot[CH_2]_3\cdot CH(CO_2Et)_2,$$

prepared from ethyl δ-bromopropylmalonate and trimethylamine, forms white, hygroscopic crystals, and, when boiled with alkali, does not yield the amine. When heated with an excess of fuming hydrobromic acid for four hours at 130°, it forms *δ-trimethylaminovaleric hydrobromide*, $NMe_3Br\cdot[CH_2]_4\cdot CO_2H$, which separates from ethyl alcohol in transparent, flat plates and melts at 184—187°. δ *Trimethylvalerobetaine*, $NMe_3<\underset{O}{\overset{[CH_2]_4}{\rule{1em}{0pt}}}>CO$, prepared by treating δ-trimethylamino-

valeric hydrobromide with freshly precipitated silver oxide, separates from ethyl alcohol in brilliant, hexagonal plates, which contain $2H_2O$ and melt at 126—127°. When dehydrated, it softens at over 200° and melts and decomposes at about 228°. Its *picrate* melts at 158—159°; its *platinichloride* melts and decomposes at 225°.

When δ-trimethylvalerobetaine is heated at 230—240°, trimethylamine is evolved and the liquid distillate consists mainly of the isomeric methyl dimethylaminovalerate, and in this respect the δ-resembles the α-betaine. The analogy, however, with γ-betaine is indicated by the presence in the distillate of small amounts of δ-valerolactone. The comportment of the δ-betaine, when heated, may accordingly be represented as follows:



The δ-valerolactone obtained was identified by its boiling point, 215° (uncorr.).

Methyl δ-dimethylamino-n-valerate, $NMe_2{\cdot}[CH_2]_4{\cdot}CO_2Me$, boils at 186—189° and has a strongly alkaline reaction; it is readily hydrolysed by contact with cold water for several days. Its *aurichloride* melts at 75°. A. McK.

Betaines. IV. Behaviour of Aromatic Betaines towards Sodium Amalgam. RICHARD WILLSTÄTTER and WALTER KAHN (*Ber.*, 1904, **37**, 1858—1860. Compare preceding abstract).—Aliphatic betaines, with the single exception of β-propiobetaine, are not acted on by sodium amalgam, even when their solutions are boiled with it; on the other hand, certain aromatic betaines are converted by sodium amalgam into the amine and acid, thus the three benzobetaines, even in the cold, are quantitatively reduced to benzoic acid and trimethylamine. Sodium amalgam has no action on phenyldimethylglycine. The reduction product from the experiments with *o*- and *p*-benzobetaines was contaminated with unsaturated hydrobenzoic acids. The amine was identified in each case by its aurichloride and platinichloride.

Aromatic amino-acids with primary, secondary, or tertiary basic groups are not attacked by sodium amalgam, with the exception of dimethylanthranilic acid, from which dimethylamine may be obtained in small amount. A. McK.

Optically Isomeric Malonobenzylamic Acids. OSCAR LUTZ (*Ber.*, 1904, **37**, 2123—2129. Compare Abstr., 1902, 596 and 698).—*l*-Bromosuccinic acid dissolved in methyl alcohol condenses with benzylamine to *benzylamine* d-*β-malonobenzylamate*, which melts at 152—153°, and has $[\alpha]_D + 31{\cdot}4°$ in methyl alcohol and $+28°$ in water. d-*β-Malonobenzylamic acid* crystallises in glistening plates, melts and decomposes at 130—131°, has a sp. gr. 1·347 at 18°/4°, and $[\alpha]_D + 13{\cdot}6°$ in methyl alcohol. The *sodium* salt has $[\alpha]_D + 33{\cdot}8°$ in water, and the *monobenzoyl* derivative melts at 125°. l-*β-Malonobenzylamic acid*,

prepared in a similar manner from *d*-chlorosuccinic acid melts at 130—131°, has a sp. gr. 1·349 at 18°/4°, and $[\alpha]_D - 13·8°$ in methyl alcohol. i-*β-malonobenzylamic acid*, prepared from *i*-bromosuccinic acid, melts at 159—160°, has a sp. gr. 1·360 at 18°/4°, forms a *benzoate* melting at 116°, and an *acetate* melting at 111°. Silver *l*-malonbenzylamate reacts with methyl iodide to form *methyl* l-*malonobenzylamate*, which crystallises in plates melting at 105°, has $[\alpha]_D - 12·8°$ in methyl alcohol, and unites with benzylamine in cold alcoholic solution to form *l*-malic acid dibenzylamide; this crystallises in plates, melts at 157°, and the saturated methyl-alcoholic solution has $[\alpha]_D - 36·9°$.

E. F. A.

Preparation of Calcium Cyanamide. Cyanid-Gesellschaft in Berlin (D.R.-P. 150878).—Calcium cyanamide is best prepared by passing nitrogen over a heated mixture of lime or other calcium compounds with carbon, an excess of carbon or carbonaceous matter being advantageous. The temperature at which the formation of cyanamide occurs is much higher than when previously prepared calcium carbide is employed (2000° instead of 800—1000°), but is below that needed for the production of carbide. C. H. D.

Preparation of Cyanides from Ferrocyanides. Grossmann's Cyanide Patents Syndicate (D.R.-P. 150551).—In the preparation of hydrocyanic acid from potassium ferrocyanide and dilute sulphuric acid, one-half of the cyanogen remains behind in the form of ferrous potassium ferrocyanide ("Everitt's salt"), and can only be very imperfectly reconverted into ferrocyanide by the action of alkali hydroxide. If, however, a slight excess of alkali hydroxide is added, and air is blown through the suspended mass, the conversion into ferrocyanide takes place rapidly and quantitatively. The remaining iron is precipitated in the form chiefly of triferric tetroxide.

C. H. D.

Chlorinated Acetonitriles. Julius Troeger and Otto Lüning (*J. pr. Chem.*, 1904, [ii], 69, 347—358. Compare Troeger, Abstr., 1895, i, 161).—Reduction of triperchloromethyltriazine (Tscherwen-Iwanoff, Abstr., 1891, 1332) by zinc dust in alcoholic solution leads to the formation of ammonia, acetic acid, and an alkaline oil which forms a crystalline *platinichloride* containing 41·98 per cent. of platinum.

When hydrogen chloride is passed through chloroacetonitrile in ethereal solution, a crystalline additive compound is formed (Weddige and Körner, Abstr., 1885, 739). This substance decomposes to chloroacetonitrile and hydrogen chloride on exposure to air. If the ether is omitted and the product preserved in a sealed tube, *chloroacetimide chloride*, $CH_2Cl·CCl:NH$, separates in crystals after some days. The action of water on chloroacetimide chloride leads to the formation of ammonium chloride and *s*-dichlorodiacetamide (König, this vol., i, 296), which melts at 195°.

Chloroacetonitrile and hydrogen bromide form an unstable *additive* compound, which decomposes on exposure to air or in a vacuum, but in a sealed tube changes into a stable *derivative*,

$$CH_2Cl·C(NH)·C(NBr)·CH_2Cl,$$

which forms white, microscopic crystals, melts at 143°, and, when acted on by water, yields *s*-dichlorodiacetamide.

With sodium *p*-tolylsulphinate in alcoholic solution, dichlorodiacetamide yields *p*-ditolylsulphonediacetamide,

$$NH(CO\cdot CH_2\cdot SO_2\cdot C_7H_7)_2,$$

which melts at 164°. G. Y.

α-Acetylamino*iso*butyronitrile. Gustaf Hellsing (*Ber.*, 1904, 37, 1921—1925).—Jay and Curtius' method for the preparation of α-aminonitriles by the action of ammonium cyanide on aldehydes (Abstr., 1894, i, 162) may also be extended to ketones.

*α-Acetylamino*iso*butyronitrile*, $CN\cdot CMe_2\cdot NHAc$, prepared by adding acetone to a solution of ammonium cyanide and adding acetic anhydride to the unstable, oily α-amino*iso*butyronitrile at first produced, crystallises from ether in transparent, rectangular tablets or needles and melts at 106°. *Potassium α-acetylamino*iso*butyrate*, $C_6H_{10}O_3NK$, obtained by hydrolysis of the nitrile, forms transparent prisms and melts and decomposes at 133°. Alcoholic hydrogen chloride converts the nitrile into *ethyl α-acetylamino*iso*butyrate*, $C_8H_{15}O_3N$, crystallising in colourless prisms and melting at 87·5°.

Alcoholic ammonium sulphide converts the nitrile into *α-acetylaminothio*iso*butyramide*, $NHAc\cdot CMe_2\cdot CS\cdot NH_2$, crystallising from water in colourless prisms, and melting and decomposing at 162°. When heated for some time above this temperature, water is evolved, and a *compound*, $C_6H_{10}N_2S$, is obtained crystallising in large, transparent leaflets, melting at 163°, and forming a yellow *hydrochloride*, which decomposes above 200°. The elimination of water may take place in one of two ways, the thioamide reacting in the amino-form, and yielding 2 : 5 ; 5-trimethyl-4-thio-4 : 5-dihydroglyoxaline,

$$\begin{matrix}N{=}CMe \\ | \\ CS\cdot CMe_2\end{matrix}\!>\!NH,$$

or in the imino-form, yielding a thiazole derivative. This point is under investigation. C. H. D.

Ethyl *iso*Cyanide Dibromide. H. Guillemard (*Bull. Soc. chim.*, 1904, [iii], 31, 605—610. Compare Tcheriac, Abstr., 1878, 132, and Nef, Abstr., 1892, 1438).—When ethyl *iso*cyanide (1 mol.), dissolved in chloroform, is treated with bromine (1 mol.) dissolved in the same solvent, *ethyl* iso*cyanide dibromide*, $NEt{:}C{:}Br_2$, is formed; this crystallises, when freed from any trace of solvent by exposure with suitable absorbents under reduced pressure, distils at 100° under 165 mm. pressure, at 93—94° under 110 mm. pressure, and at 145—147° under atmospheric pressure; if, however, the latter temperature be exceeded, decomposition ensues with the formation of a black, resinous residue and a white, crystalline sublimate.

Water converts the dibromide into ethylamine hydrobromide. With hydrogen sulphide, *ethyl* iso*cyanide dibromide hydrobromide* and ethylthiocarbimide are formed. The latter is also obtained by the action of metallic sulphides. Dry hydrogen chloride passed through a solution of the dibromide in carbon disulphide, furnishes the *hydrochloride*, which, like the hydrobromide, is colourless and

crystalline. With ethyl iodide, an oily *ethiodide* is produced. The action of alcohol on the dibromide dissolved in carbon disulphide is similar to that of water, but there are also formed ethyl bromide and ethylcarbimide hydrobromide. With mercuric oxide, ethylcarbimide is produced. When dry ammonia is passed into a solution of the dibromide in chloroform, ammonium bromide is precipitated and a *base*, $C_6H_{12}N_4$ is formed, which crystallises in colourless needles, melts at 90—94°, is soluble in alcohol, insoluble in water and benzene, and furnishes crystalline *salts* and a slightly soluble *picrate* and *platinichloride*. To this product, the author assigns the formula

$$NEt\dot{:}C<^{NH}_{NH}>C\dot{:}NEt.$$

Similar substances are produced with methylamine and aniline.

T. A. H.

Diazo-fatty Acids. Angelo Angeli (*Ber.*, 1904, 37, 2080—2081).—A claim for priority (compare Abstr., 1893, i, 261, and Curtius and Müller, this vol., i, 481). J. J. S.

Diazotisation of Hydrazine. II. Mario Betti (*Gazzetta*, 1904, 34, i, 201—212. Compare Abstr., 1903, i, 78).—*Bisdiazoacetone*, $N_4(CH_2Ac)_2$, obtained in place of ethyl bisdiazoacetoacetate (*loc. cit.*), under certain conditions of diazotisation of hydrazine in presence of ethyl acetoacetate, crystallises from alcohol in golden-yellow, silky needles, melts and decomposes at 228° and is soluble in methyl or amyl alcohol or acetone and, with partial decomposition, in water. It sublimes, with slight decomposition, yielding white, silky crystals which have the melting point 228°, and forms yellow needles when crystallised from alcohol. It is soluble in moderately concentrated alkali hydroxide solution, from which it is precipitated unchanged by the addition of acid. The *sodium* salt, $C_6H_8O_2N_4Na_2$, yields a strongly alkaline aqueous solution which gives precipitates with various metallic salts. Its *dibenzoyl* derivative, $N_4(CHBzAc)_2$, crystallises from alcohol in long, golden needles melting at 170°. Bisdiazoacetone has the normal molecular weight in boiling ethyl acetate solution. When boiled with dilute hydrochloric acid, it yields nitrosoacetone, acetone, and a large proportion of methylglyoxime.

Under still other conditions of diazotisation, in presence of ethyl acetoacetate, hydrazine yields: (1) a small proportion of ethyl bisdiazoacetoacetate and

(2) *Ethyl azodiazobisacetoacetate*,

$$CO_2Et\cdot CHAc\cdot N\dot{:}N\cdot N\dot{:}CMe\cdot CH_2\cdot CO_2Et,$$

which crystallises from aqueous alcohol in pale greenish-yellow, nacreous, rhombohedral plates melting and decomposing at 140°. It has an acid reaction and exhibits normal ebullioscopic behaviour in benzene. With hydrochloric acid, it yields, like ethyl bisdiazoacetoacetate, *iso*nitrosomethylpyrazolone. T. H. P.

Basic Properties of Cacodylic Acid and of Carbamide. Jan von Zawidzki (*Ber.*, 1904, 37, 2289—2298. Compare this vol., i, 232; Hantzsch, this vol., i, 381).—That cacodylic acid has no dibasic tendency is shown by a comparison with carbonic acid, a weak,

dibasic acid which has a dissociation constant ($K = 3{\cdot}04 \times 10^{-7}$ for $HCO_3{\cdot}H$) similar to that of cacodylic acid ($K = 4{\cdot}2 \times 10^{-7}$). On mixing solutions of potassium hydrogen carbonate and potassium hydroxide, the electrical conductivity is 56·4 per cent. less than that calculated by a simple additive rule, whereas in the case of sodium cacodylate the decrease is 10 per cent., with sodium chloride, 4 per cent., and with sodium acetate 5·5 per cent.

No conclusion as to the character of the basicity of cacodylic acid can be drawn from a comparison with dimethylpyrone, as the basic nature of the latter is equally unexplained. From its accelerating effect on the bi-rotation of lactose, the dissociation constant of cacodylic acid as a base is found to be $1{\cdot}35 \times 10^{-13}$. This agrees well with the dissociation constants for cacodylic acid calculated from the hydrolysis of its hydrochloride, and from its effect on the bi-rotation of dextrose. It is shown that there is a similar agreement between the dissociation constants for carbamide obtained by these different methods.

Abnormal temperature coefficients for the dissociation constants of weak bases are not uncommon. For carbamide at 25°, $K = 1{\cdot}5 \times 10^{-14}$; at 40·2°, $K = 3{\cdot}7 \times 10^{-14}$ (Wood, Trans., 1903, 83, 568). G. Y.

Substitution in the Benzene Nucleus. Jan J. Blanksma (*Rev. trav. chim.*, 1904, 23, 202—217. Compare Armstrong, Trans., 1887, 51, 258, and 1900, 77, 104; Crum Brown and Gibson, *ibid.*, 1892, i, 61, 367; Chattaway and Orton, *ibid.*, 1901, 79, 274; Vorländer, Abstr., 1902, i, 328; Flürscheim, Abstr., 1903, i, 79; and Holleman, Abstr., 1903, i, 623).—The author has already given expression to the view, which is in harmony with the ideas enunciated by Hantzsch, Bamberger, and Chattaway and Orton, that direct substitution in the benzene nucleus gives rise to the formation (principally) of meta-compounds, and indirect substitution to a mixture of ortho- and para-derivatives (Abstr., 1902, i, 600. Compare Lobry de Bruyn, this vol., i, 388). In extension of this, he now suggests that the following rule is generally applicable. When the nucleus contains two or three of any one of the groups NH_2, OH, or Me or any possible combinations by twos or threes of these three groups in the positions 1, 3, and 5, it is possible to introduce under determinate conditions the groups Me, $CH_2{\cdot}OH$, CH_2Cl, CHO, $CHCl_2$, CO_2H, CCl_3, Ac, Bz, HSO_3, I, Br, Cl, NO_2 or NO or N:NPh, &c., and so much the more easily as there are more of the groups Me, NH_2, and OH present in the nucleus. Conversely, the elimination of certain groups is similarly favoured by the number of Me, NH_2, or OH groups present in the nucleus.

A large number of illustrative instances of the applicability of this rule are given in the original. T. A. H.

Interaction occurring between Aluminium, Mercuric Chloride, and Benzene. Wladimir von Gulewitsch (*Ber.*, 1904, 37, 1560—1564).—When aluminium turnings are added in a reflux apparatus to benzene containing mercuric chloride, a very vigorous

action occurs; on slow evaporation of the filtered product, large, transparent, six-sided plates separate which have the composition $C_6H_6,AlCl_3,HgCl$; the compound formed is hygroscopic, and is decomposed by water giving benzene, mercurous chloride, and some mercury.

In the formation of the compound, mercurous chloride is initially produced according to the equation: $3Al + 6HgCl_2 = 3AlCl_3,HgCl + 3Hg$; the amount of mercury liberated corresponds sufficiently closely with that required by theory. A similar interaction occurs with the hydrocarbons, toluene, ethylbenzene, the three xylenes, cumene, ψ-cumene, mesitylene, and cymene, which are all solvents for mercuric chloride; carbon disulphide and the hydrocarbons, hexane and decane, which do not dissolve mercuric chloride, fail to bring about an interaction between aluminium and mercuric chloride. W. A. D.

Haloid Substitution in some Nitro-Halogenated Substances. Jan J. Blanksma (*Rec. trav. chim.*, 1904, 23, 125—130).—When *s*-dibromotoluene is slowly added to four times its weight of nitric acid of sp. gr. 1·52 and the mixture warmed for 10 minutes at 100°, there is formed a product crystallising in cubes and melting at 106—108° (already obtained by Neville and Winther, Trans., 1880, 37, 431, in addition to 3 : 5-*dibromo*-2 : 4-*dinitrotoluene*, which crystallises in needles and melts at 157°. The latter reacts with ammonia and amines less readily than 1 : 3-dibromo-4 : 6-dinitrobenzene, but when dissolved in alcohol and heated with appropriate amines in closed tubes at 150°, the following substances are formed: 2 : 4-*dinitro*-3 : 5-*diaminotoluene*, yellow crystals melting at 199°; 2 : 4-*dinitro*-3 : 5-*di-methylaminotoluene*, bright red crystals melting at 140°, and 2 : 4-*dinitro*-3 : 5-*dianilinotoluene*, red crystals melting at 162°. The product melting at 106—108° appears to be a mixture of 3 : 5-dibromo-2 : 4-dinitrotoluene with an isomeride.

3 : 5-Dibromo-2 : 4 : 6-trinitrotoluene, prepared by nitrating dibromotoluene in presence of sulphuric acid, reacts readily with ammonia and amines. 2 : 4 : 6-*Trinitro*-3 : 5-*di-methylaminotoluene*, so prepared, forms red crystals, melts at 156°, and, with nitric acid of sp. gr. 1·52, is converted into 2 : 4 : 6-*trinitro*-3 : 5-*di-methylnitroaminotoluene*, which may also be obtained by nitrating the dinitrodi-methylaminotoluene already described; it forms colourless crystals and melts and decomposes at 199—200°. 2 : 4 : 6-*Trinitro*-3 : 5-*dianilinotoluene* forms pale red crystals and melts at 206°; the corresponding *toluidine* derivative is also red and melts at 185°.

When the 3 : 5-dibromo-2 : 4 : 6-trinitrotoluene or 3 : 5-dibromo-2 : 4-dinitrotoluene is treated with sodium methoxide, only resinous products are formed, due apparently to the oxidation of the methyl group by the nitro-group in the *ortho*-position, since 2 : 4 : 6-tribromo-3 : 5-dinitrotoluene, although the reactivity of its bromine atoms is diminished by the presence of the methyl group, furnishes, with sodium methoxide and methyl alcohol at 100° a crystalline product composed of a mixture of a mono- with a dibromo-derivative.

s-Tribromodinitrobenzene, prepared by Loring Jackson's method, reacts with methylamine to form 2 : 4-*dinitro*-1 : 3 : 5-*trimethylaminobenzene*, which forms orange-red crystals, melts at 220°, and is

converted by nitric acid into s-*trinitrotri-methylnitroaminobenzene*, which is colourless, crystallises from acetic acid and explodes at 200—203°, occasionally bursting into flame simultaneously. T. A. H.

Preparation of Salts of Sulphamic Acids of Benzene and its Homologues. Hugo Weil (D.R.-P. 151134).—Nitrobenzene and its homologues are readily reduced by solutions of hydrogen sulphites, the principal products being sulphamates, together with small quantities of aminosulphonates, the yield of the former increasing with the number of alkyl groups in the benzene ring. The reaction proceeds according to the equation: $ArNO_2 + 3NaHSO_3 = NHAr{\cdot}SO_3Na + 2NaHSO_4$, or, when neutral sulphite is added $ArNO_2 + NaHSO_3 + 2Na_2SO_3 = NHAr{\cdot}SO_3Na + 2Na_2SO_4$. In practice, calcium hydrogen sulphite is the most convenient reagent. The reaction only takes place in dilute solution, and this is perhaps the reason why it has hitherto been overlooked. The alkali sulphamates are precipitated from their solutions by the addition of sodium chloride, and when recrystallised from 95 per cent. alcohol, form well-developed crystals.

The sulphamic acids derived from *p*-toluidine and the xylidines may be precipitated from solutions of their sodium salts by dilute hydrochloric acid. Their melting points vary according to the rate of heating. Boiling dilute acids readily hydrolyse them to aminosulphonic acids. C. H. D.

Preparation of Alkylsulphinic Acids. Arthur Rosenheim and Ludwig Singer (*Ber.*, 1904, 37, 2152—2154).—The following acids were prepared by the action of sulphur dioxide on ethereal solutions of magnesium alkyl haloids.

Magnesium ethylsulphinate crystallises in glistening, colourless flakes, *magnesium propylsulphinate* in colourless plates, *magnesium benzenesulphinate*, $2Mg(PhSO_2)_2,PhSO_2{\cdot},6H_2O$, as a microcrystalline powder, and the normal *sodium* and *silver* benzenesulphinates in colourless plates and needles respectively, whilst benzenesulphinic acid forms stellar aggregates of colourless prisms melting at 84°. o-Toluenesulphinic acid and naphthalene-α-sulphinic acid can be obtained in a similar manner. E. F. A.

Styrenes. VI. August Klages (*Ber.*, 1904, 37, 2301—2317. Compare Abstr., 1902, i, 611, 666; 1903, i, 19; this vol., i, 302, 497). —The term "styrolene" is introduced by the author to designate those styrenes which possess an additional double linking in the side-chain; a "styrodiene" possesses two double linkings in the side-chain, and a "styrotriene" three. The present communication deals mainly with $\Delta^{1,2}$- and $\Delta^{1,3}$-styrolenes.

αγ-Dimethyl-Δ^{αβ}-butadienyl-benzene (*phenyltrimethylallene*),

$$CMePh{:}C{:}CMe_2,$$

prepared from mesityl oxide and magnesium phenyl bromide, is a strongly refracting oil with an odour of lemons and boils at 107—108° under 20 mm. pressure, has a sp. gr. 0·9277 at 19·8°/4° and n_D 1·5236. The tertiary alcohol, resulting as the primary product of the Grignard reaction in question, appears to lose water with great ease. When

oxidised either by potassium permanganate and sulphuric acid or by chromic acid, phenyltrimethylallene forms acetophenone, which was identified by its phenylhydrazone and its semicarbazone. *Phenyltrimethylallene tetrabromide*, prepared by the action of bromine on the hydrocarbon at 0°, is an inodorous syrup. When the hydrocarbon is reduced by sodium and alcohol, it forms *$\alpha\gamma$-dimethyl-Δ -butenylbenzene*, CHMePh·CH:CMe$_2$, a colourless liquid with an odour of geranium; it boils at 98—100° under 19 mm. pressure and at 210—211° under 755 mm. pressure, has a sp. gr. 0·8931 at 20°/4° and n_D 1·5162; its *nitrosylchloride* melts at 140°. In order to prove that, during its formation from trimethophenylallene, the addition of hydrogen occurred at the Δ^α- and not at the Δ^β-position, where the double linking is retained, the compound, which would have been formed had the addition of hydrogen occurred at the Δ^β-position and where the double linking in the Δ^α-position is retained, was prepared by the action of magnesium *iso*butyl iodide on acetophenone, namely, *$\alpha\gamma$-dimethyl-Δ^α-butenylbenzene*, CMePh:CH·CHMe$_2$; it is a mobile oil and boils at 99—101° under 20 mm. pressure, has a sp. gr. 0·8498 at 15°/4° and n_D 1·516; that this compound was actually a Δ^α-hexenylbenzene was proved by its conversion during reduction into sec-*hexylbenzene* [*$\alpha\gamma$-dimethylbutylbenzene*], CHMePh·CH$_2$·CHMe$_2$, a mobile oil, boiling at 77° under 9 mm. pressure, having a sp. gr. 0·8634 at 15°/4° and n_D 1·4876, and forming crystalline *barium, sodium, magnesium,* and *copper sulphonates.*

From the action of magnesium *iso*butyl iodide on acetophenone, the primary product *dimethobutylolbenzene* [α-hydroxy-$\alpha\gamma$-dimethylbutylbenzene], CMePh(OH)·CH$_2$·CHMe$_2$, was isolated; it is a syrupy, almost inodorous oil, and boils at 110—112° under 12 mm. pressure.

1-Phenyl-$\Delta^{\alpha\gamma}$-butadiene, CHPh:CH·CH:CH$_2$, the preparation of which from styrylmethylcarbinol has previously been described by the author, may also be prepared by the action of an excess of magnesium methyl iodide on cinnamaldehyde (compare von der Heide, this vol., i, 583). When reduced by sodium and alcohol, it forms *α-phenyl-Δ^β-butylene* (*Δ^β-butenylbenzene*), CH$_2$Ph·CH:CHMe, a mobile oil which boils at 176° under 765 mm. and at 76° under 18 mm. pressure, and has a sp. gr. 0·8857 at 15°/4° and n_D 1·5109 at 15°. Its constitution was established by its forming phenylacetaldehyde when oxidised by ozone (Harries). When heated with alcoholic potassium hydroxide at 160—180°, it undergoes rearrangement, the double linking shifting from the Δ^β- to the Δ^α-position; phenyl-Δ^α-butylene dibromide was isolated. α-Phenyl-Δ^α-butylene, CHPh:CHEt, was then reduced to n-butylbenzene.

Phenylpropylcarbinol, CHPrPh·OH, prepared by the action of magnesium propyl iodide on benzaldehyde, is a colourless oil which has a sp. gr. 1·0212 at 18°/4°, and boils at 110° under 15 mm. pressure. When its *chloride*, which is a colourless oil, boiling and decomposing at 94° under 20 mm. pressure, is heated with pyridine at 125°, *α-phenyl-Δ^α-butylene* (*Δ^α-butenylbenzene*), CHPh:CHEt, is formed; it boils at 89—90° under 15 mm. and at 189° at the ordinary pressure, and has a sp. gr. 0·9124 at 16°/4° and n_D 1·5414. It accordingly possesses a higher specific gravity, a higher boiling point and a higher molecular refraction than its isomeride of the Δ^β-series.

γ-Hydroxybutylbenzene, $CH_2Ph\cdot CH_2\cdot CHMe\cdot OH$, prepared by the reduction of benzylacetone with sodium and alcohol, boils at 236—238°, has a sp. gr. 0·9899 at 16·5°/4°, and n_D 1·517 at 16·5°; its *phenylurethane* separates from alcohol in colourless needles and melts at 113°.

γ-Hydroxy-γ-methylbutylbenzene, $CH_2Ph\cdot CH_2\cdot CMe_2\cdot OH$, prepared by the action of magnesium methyl iodide on benzylacetone, boils at 121° under 13 mm. pressure; its *phenylurethane* separates from alcohol in glistening needles and melts at 143—144°. By the action of hydrochloric acid and pyridine, it is converted into α-phenyl-γ-methyl-Δ^β-butylene, $CH_2Ph\cdot CH{:}CMe_2$, which boils at 92° under 15 mm. and at 205° under the ordinary pressure. That this product was identical with the amenylbenzene previously described by the author was shown by the identity of the dibromides and nitrosochlorides prepared from the respective styrenes, which moreover were identical in physical properties and yielded the same α-phenyl-γ-methyl-Δ^α-butylene when boiled with alcoholic potassium hydroxide: in both cases, the same products are formed when oxidation by ozone is effected (Harries), thus: $CH_2Ph\cdot CH{:}CMe_2 \rightarrow Ph\cdot CH_2\cdot CHO + COMe_2$. The transformation of α-phenyl-γ-methyl-Δ^β-butylene into the isomeric Δ^α-compound takes place slowly at 180° under the influence of alcoholic potassium hydroxide. The Δ^α-styrene, in contradistinction to the Δ^β-isomeride, which is not capable of being reduced, is converted by sodium and alcohol into *iso*amylbenzene.

Phenyl-iso*butylcarbinol*, $OH\cdot CHPh\cdot CH_2\cdot CHMe_2$, boils at 126° under 21 mm. pressure, and has a sp. gr. 0·9567 at 17°/4°; when its chloride is heated with pyridine, it forms α-phenyl-γ-methyl-Δ^α-butylene, $CHPh{:}CH\cdot CHMe_2$, which boils at 102—103° under 26 mm., at 207° under 757 mm. pressure, has a sp. gr. 0·8903 at 14·6°/4°, and n_D 1·5248. The *dibromide* of the latter compound melts at 128°. When α-phenyl-γ-methyl-Δ^α-butylene is reduced, it forms *iso*amylbenzene, boiling at 198—199° under 757 mm. pressure.

γ-Hydroxy-γ-methylamylbenzene, $CH_2Ph\cdot CH_2\cdot C(OH)MeEt$, prepared by the action of magnesium ethyl iodide on benzylacetone, boils at 129—130° under 13 mm. pressure and has a sp. gr. 0·9690 at 15·3°/4°. Its *phenylurethane* melts at 94—95°. When the chloride of the carbinol just described is heated with pyridine at 125°, *α-phenyl-γ-methyl-Δ^β-pentene*, $CH_2Ph\cdot CH{:}CMeEt$, is formed; this boils at 103—104° under 15 mm. and at 226° under 749 mm. pressure, has a sp. gr. 0·9004 at 18°/4° and $n_D = 1·5100$ at 18°, and cannot be reduced by sodium and alcohol. Its *nitrosochloride* separates from alcohol in glistening needles and melts and decomposes at 140—141°. A. McK.

Bisdiphenylbutadiene. C. N. Riiber (*Ber.*, 1904, 37, 2272—2276. Compare Liebermann and Riiber, Abstr., 1902, i, 669; Doebner and Staudinger, this vol., i, 149).—Oxidation of bisdiphenylbutadiene with potassium permanganate in acetone solution at 20—25° leads to the formation of benzoic acid and a *tribasic acid*, $C_{13}H_{12}O_6$. This tribasic acid crystallises in needles, melts and effervesces at 184°, and is soluble in acetone, but only slightly so in other solvents. When distilled under 3 mm. pressure, it yields a gelatinous anhydride (?) which is

soluble in ether. The *methyl* ester distils at 200° under 0·3 mm. pressure. When heated with potassium permanganate in sulphuric acid solution, the acid is oxidised with formation of benzoic acid.

With bromine in carbon disulphide solution, bisdiphenylbutadiene forms a *tribromo*-derivative, $C_{20}H_{19}Br_3$, which melts and decomposes at 223°. It is easily soluble in boiling benzene or chloroform, but only slightly soluble in other solvents. It is not oxidised by potassium permanganate in acetone solution.

The author considers the structure of bisdiphenylbutadiene to be

$$\begin{array}{l} CH_2\cdot CH\cdot CHPh \\ CH_2\cdot CH\cdot CH\cdot CH{:}CHPh \end{array} \quad \text{or} \quad \begin{array}{l} CH_2 - CH \\ \quad CHPh \\ CH_2 - CH \end{array} \!\!> CH\cdot CH{:}CHPh.$$

The tribasic acid would be

$$\begin{array}{l} \quad\;\; CHPh\cdot CH\cdot CO_2H \\ CO_2H\cdot CH - CH\cdot CO_2H \end{array}$$

G. Y.

Derivatives of Hexaphenyl-*p*-xylene. FRITZ ULLMAN and CARL SCHLAEPFER (*Ber.*, 1904, 37, 2001—2008).—*Tetraphenyl*-p-*xylylene glycol*, $C_6H_4(CPh_2\cdot OH)$, prepared by the action of magnesium phenyl bromide on methyl terephthalate in ethereal solution, separates from benzene as a crystalline powder and melts at 169°; in boiling benzene solution, it is converted by gaseous hydrogen chloride into *tetraphenyl*-p-*xylylene chloride*, $C_6H_4(CPh_2Cl)$, which melts at 247° and interacts with aniline, giving *dianilinotetraphenyl*-p-*xylene*, $C_6H_4(CPh_2\cdot NHPh)_2$. This substance crystallises from benzene in white leaflets and melts at 225°. The isomeric 4′ : 4′- *diaminohexaphenyl*-p-*xylene*,

$$C_6H_4(CPh_2\cdot C_6H_4\cdot NH_2)_2,$$

is formed when tetraphenyl-*p*-xylylene glycol is heated with aniline hydrochloride and glacial acetic acid; it forms an indistinctly crystalline powder, melts at 358°, and is sparingly soluble in most solvents; the *dihydrochloride*, $C_{44}H_{38}N_2Cl_2$, melts at 355°, and the *diacetyl* derivative, $C_{48}H_{40}O_2N_2$, crystallises from xylene and melts at 231°.

4′ : 4′-*Diamino*-3′ : 3′-*dimethylhexaphenyl*-p-*xylene*,

$$C_6H_4(CPh_2\cdot C_6H_3Me\cdot NH_2)_2,$$

prepared from tetraphenyl-*p*-xylylene glycol and *o*-toluidine hydrochloride, crystallises from xylene and melts at 277°; the *dihydrochloride* melts at 259°. 4 : 4′-*Dimethylamino*-3 : 3′-*dimethylhexaphenyl*-p-*xylene*, $C_6H_4(CPh_2\cdot C_6H_3Me\cdot NHMe)_2$, obtained by using methyl-*o*-toluidine, forms a white, crystalline powder and melts at 287°.

Tetraphenyl-p-*xylene*, $C_6H_4(CHPh_2)_2$, prepared by reducing tetraphenyl-*p*-xylylene glycol with zinc dust and glacial acetic acid, crystallises from the acid in white needles and melts at 172°.

4′ : 4′-*Dihydroxyhexaphenyl*-p-*xylene*, $C_6H_4(CPh_2\cdot C_6H_4\cdot OH)_2$, prepared by adding concentrated sulphuric acid to a mixture of phenol and tetraphenyl-*p*-xylylene glycol in glacial acetic acid, crystallises in small colourless prisms and melts at 304°. A similar condensation with salicylic acid could not be effected.

W. A. D.

Formation of Chloroanilines. EYVIND BOEDTKER (*Compt. rend.*, 1904, 1174—1175).—*p*-Chloroaniline is sometimes formed during the

reduction of nitrobenzene with tin and hydrochloric acid. The reaction is expressed by the equation : $C_6H_5 \cdot NO_2 + HCl + 2H_2 = C_6H_4Cl \cdot NH_2 + 2H_2O$. S. S.

Action of Bromine on the Salts of Aromatic Amines with Halogen Hydrides. K. FRIES (*Ber.*, 1904, 37, 2338—2346).—The primary products resulting from the action of bromine on the salts of aromatic amines with halogen hydrides are additive compounds, the transformation of which into substitution derivatives takes place with ease in the cases of compounds of primary and secondary amines. The perbromides of tertiary amines, where the para- and ortho-positions relatively to the amino-group are free, exhibit considerable tendency to transformation into substitution products; where the para-position, however, is substituted, the compounds in question are very stable.

p-*Bromodimethylaniline hydrobromide perbromide*,

$$C_6H_4Br \cdot NMe_2,HBr,Br,$$

prepared from *p*-bromodimethylaniline hydrobromide (2 mols.) and bromine (1 mol.), crystallises from glacial acetic acid in long, dark red prisms, which soften at 95° and melt at 107°. *p*-Bromodimethylaniline is formed by the action of acetone or sodium hydrogen sulphite on this compound, whilst with sodium acetate a mixture of equal parts of monobromo- and dibromo-dimethylanilines results. The *compound*,

$$C_6H_4Br \cdot NMe_2,HBr,Br_2,$$

prepared from *p*-bromodimethylaniline hydrobromide (1 mol.) and bromine (1 mol.), separates from glacial acetic acid in dark red plates and melts at 70—75°. It behaves towards acetone, sodium hydrogen sulphite, and sodium acetate like the compound first described. Water converts it into dibromodimethylaniline and *tetramethylbenzidine hydrobromide perbromide*, $C_{12}H_8(NMe_2)_2,2HBr,Br_4$; the latter melts at about 158° with evolution of hydrogen bromide; with sodium hydrogen sulphite, it forms tetramethylbenzidine.

o-p-*Dibromodimethylaniline hydrobromide perbromide*,

$$(C_6H_3Br_2 \cdot NMe_2,HBr)_2Br,$$

prepared from dibromodimethylaniline hydrobromide and bromine in glacial acetic acid solution, forms plates with a greenish-black lustre and melts and decomposes at 135°. The *compound*

$$C_6H_3Br_2 \cdot NMe_2,HBr,Br_2,$$

prepared from *o-p*-dibromodimethylaniline hydrobromide (1 mol.) and bromine (1 mol.), crystallises in prisms and melts at 102°.

as-m-*Xylidine hydrobromide perbromide*, $C_6H_3Me_2 \cdot NH_3Br,Br_2$, forms bromo-xylidine when acted on by water; it readily parts with bromine at the ordinary temperature, xylidine hydrobromide being left.

Bromo-as-m-*xylidine hydrobromide perbromide*,

$$C_6H_2BrMe_2 \cdot NH_3Br,Br_2,$$

forms red plates and melts and decomposes at 134°. On exposure to air, bromine is separated and bromoxylidine hydrobromide regenerated.

o-p-*Dibromomethylaniline hydrobromide perbromide*,

$$C_6H_3Br_2 \cdot NH_2MeBr,Br,$$

forms yellowish-red, triclinic pyramids and melts and decomposes at 125°. It is comparatively stable and parts with bromine only after several days' exposure to air; it may be recrystallised from glacial

acetic acid containing a little hydrobromic acid. When its solution in glacial acetic acid is warmed, a mixture of dibromo- and tribromomethylanilines is produced. A. McK.

Action of Phosphorus Trichloride on some Primary Cyclic Amines at the Boiling Point; Reduction of Phosphorus Trichloride with Formation of Phosphorus. PAUL LEMOULT (*Compt. rend.*, 1904, 138, 1223—1225. Compare Abstr., 1903, i, 672; this vol., i, 380).—The action of phosphorus trichloride on cyclic amines has been studied by Jackson and Mencke (Abstr., 1885, 254), and by Hinzberg (Abstr., 1894, i, 580), who found that in addition to the arylamides of phosphoric acid, hydrogen phosphide and a red amorphous substance, probably red phosphorus, were also formed. The author, however, finds that when 1 mol. of phosphorus trichloride is gradually added to 8 mols. of aniline dissolved in benzene, ether, or chloroform there is a vigorous action, and aniline hydrochloride is formed; on distilling off the solvent and heating the residual liquid to boiling for several days, an orange-red solid is deposited, and there is a strong odour of phosphorus, but no gas is evolved. The residual solid consists of diphenylamine, the anilide of phosphoric acid, $PO(NHPh)_3$, the compound $PCl(NHPh)_4$, and an insoluble red substance containing 85 per cent. of phosphorus; if the heating be discontinued directly the red solid begins to separate, white phosphorus can be extracted by means of carbon disulphide from the mixture. With the exception of the diphenylamine, the crystalline products are the same as those obtained by the action of phosphorus pentachloride on aniline, and it is probable therefore that the phosphorus trichloride is converted into the pentachloride and free phosphorus according to the equation $5PCl_3 = 3PCl_5 + P_2$. Similar series of compounds are obtained when methylaniline, *o*- or *p*-toluidine, or xylidine are used instead of aniline. M. A. W.

Preparation of Phenylaminoacetonitrile. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 151538).—Phenylaminoacetonitrile, $NHPh\cdot CH_2\cdot CN$, was obtained by Miller and Plöchl (Abstr., 1892, 1189) by the action of dry hydrogen cyanide on anhydroformaldehydeaniline, $C_6H_5\cdot N\colon CH_2$. It is more conveniently prepared by mixing aniline, formaldehyde, potassium cyanide, and a mineral acid in molecular proportion in aqueous or alcoholic solution.

C. H. D.

Piria's Thionaphthamic Acid and the Products of the Action of Aminosulphonic Acid on α-Naphthylamine. Preparation of α-Aminonaphthalene-2-sulphonic Acid. J. C. RUIJTER DE WILDT (*Rec. trav. chim.*, 1904, 23, 173—186).—The author confirms the statement of Piria (*Annalen*, 1851, 78, 54) that when α-nitronaphthalene, dissolved in alcohol, is treated with an aqueous solution of sodium sulphite, α-naphthylsulphamic acid is produced. He has also repeated the experiments of Paal and Jaenecke (Abstr., 1896, i, 235), and finds that when α-naphthylamine is treated with

amidosulphonic acid by the method recommended by these authors the principal product is a mixture of the 1 : 2- and 1 : 4-naphthylaminesulphonic acids, and not, as they assert, a stable α-naphthylsulphamic acid. The 1 : 2-naphthylaminesulphonic acid was separated from the mixture by precipitation as the barium salt (which forms brilliant, white scales) and regeneration from this. It crystallises in long needles and melts and decomposes at 262—265° (compare Erdmann, Abstr., 1893, i, 653 and 655). When the silver salt is heated in closed tubes at 100° with ethyl iodide, *1-ethylaminonaphthalene-2-sulphonic acid* is formed; this crystallises from water in needles and melts at 207—208°. It is soluble in strong acids and is reprecipitated from its solution in hydrochloric acid on addition of water. The *potassium*, *barium*, *lead*, and *silver* salts are very soluble in water.

Piria's acid may, however, be obtained by mixing aminosulphonic acid with α-naphthylamine and warming the mixture to 85—95°, when a slight turbidity appears. If the heating is then discontinued, the temperature rises spontaneously to 100—113° and the liquid solidifies. From the mass, the acid may be obtained by washing first with a mixture of ether and benzene, then with ether alone, and finally converting into the potassium salt. The acid may also be obtained by the action of chlorosulphonic acid on α-naphthylamine dissolved in chloroform or carbon tetrachloride. T. A. H.

Oxygen Ethers of Carbamide. W. M. BRUCE (*J. Amer. Chem. Soc.*, 1904, 26, 449—464. Compare this vol., i, 491).—*O-Methyl diphenyldiureido*iso*carbamide*, NHPh·CO·NH·C(OMe):N·CO·NHPh, prepared from methyl phenyl*iso*biuret and phenylcarbimide, melts at 153°. When treated with dry hydrogen chloride at 60°, it forms *carbonyl diphenyldicarbamide*, $(NHPhCO·NH)_2CO$, which melts at 211°. *O-Methyl carbethoxy*iso*carbamide*, $OEt·CO·N:C(OMe)·NH_2$, prepared from methyl *iso*carbamide hydrochloride, potassium hydroxide, and ethyl chlorocarbonate, melts at 5°. When hydrogen chloride is passed into the dry ethereal solution of the preceding compound, ethyl allophanate is formed, *O*-methyl carbethoxy*iso*carbamide hydrochloride readily parting with methyl chloride.

*O-Methyl thiophenylureido*iso*carbamide*, $NHPh·CS·N:C(OMe)·NH_2$, prepared from methyl *iso*carbamide and phenylcarbimide, separates from benzene in diamond-shaped plates and melts at 131°. *O-Methyl* iso*biuret*, $NH_2·CO·N:C(OMe)·NH_2$, prepared from methyl *iso*carbamide hydrochloride and potassium *iso*cyanate, melts at 118°. When treated with dry hydrogen chloride, methyl chloride is evolved and biuret produced.

*Benzylidenedimethyldi*iso*carbamide*, $CHPh[NH·C(OMe):NH]_2$, formed from methyl *iso*carbamide and benzaldehyde, melts at 137°; small quantities of tribenzylidenetetra*iso*carbamide are also formed. When benzylidenedimethyldi*iso*carbamide is treated with dry hydrogen chloride, benzylidenediureide is produced. *Benzylidenediethyldi*iso*carbamide*, $CHPh:[NHC(OEt):NH]_2$, prepared from ethyl *iso*carbamide and benzaldehyde, melts at 154°.

By condensation of *iso*carbamide ethers with esters of β-ketonic acids, oxygen ethers of 2-hydroxypyramidines are readily formed

6-*Hydroxy-2-methoxy-4-methylpyrimidine*, $N\lessdot\begin{matrix}C(OMe)-N\\C(OH):CH\end{matrix}\gtrdot CMe$, prepared from methyl *iso*carbamide and ethyl acetoacetate, separates from alcohol in feathery masses of needles and melts at 207°. Its hydrochloride readily evolves methyl chloride with the formation of methyluracil. 6-*Hydroxy-2-ethoxy-4-methylpyrimidine* separates from ethyl alcohol in shining needles and melts at 206°. 6-*Hydroxy-2-methoxy-4-methyl-5-ethylpyrimidine*, prepared from methyl *iso*carbamide and ethyl acetoacetate, separates from ethyl alcohol in needles and melts at 210°. O-*Methyl oxalyl*iso*carbamide* (*μ-methyl parabanic acid*), $OMe\cdot C\lessdot\begin{matrix}N\cdot CO\\NH—\end{matrix}\gtrdot CO$, prepared from methyl *iso*carbamide and ethyl oxalate, separates from ethyl alcohol in three-sided prisms and melts at 137·5°. Its hydrochloride readily decomposes to form oxalylurea.

The affinity constants of various *iso*carbamides were determined. With methyl *iso*carbamide, there is practically no hydrolysis where $v = 1024$; the molecular conductivity at infinite dilution = 239·6. The results, obtained with methyl *iso*carbamide, are contrasted with those obtained by Walker for carbamide. Methyl *iso*carbamide is a stronger base than carbamide, its affinity constant being $6{\cdot}4 \times 10^{-5}$, a value of the same order as that of ammonia. The molecular conductivity of ethyl *iso*carbamide at infinite dilution is 234·6. Ethyl *iso*carbamide is nearly twice as strong a base as methyl *iso*carbamide. The substitution of an ethyl for a methyl group attached to oxygen causes a much more decided increase in the affinity constant than is the case when a similar single substitution is effected for a methyl group attached to nitrogen. The molecular conductivity of methyl phenyl*iso*carbamide at infinite dilution is 225·5; the affinity constant of methyl phenyl*iso*carbamide is 1/300 that of methyl *iso*carbamide. The molecular conductivity of ethyl phenyl*iso*carbamide at infinite dilution is 224·2; the substitution of the ethyl for the methyl group doubles the strength of the base. A. McK.

Constitution of Aromatic Purpuric Acids. V. The Purpurate Reaction with 2:4-Dinitrophenols. WALTHER BORSCHE and E. BÖCKER (*Ber.*, 1904, **37**, 1843—1853. Compare this vol., i, 166).—Purpurate formation does not take place with mononitrophenols and potassium cyanide. At least two nitro-groupings must be present in the phenol molecule; those must be in the meta-position to one another, and at least one of them must be contiguous to the phenolic hydroxyl group. Purpurates are accordingly sharply differentiated into two classes, according as they are derived from 2:4- or 2:6-dinitrophenols. The present research deals with purpurate formation from 2:4-dinitrophenols.

Potassium metapurpurate (potassium 4-nitro-2-hydroxylamino-3-cyanophenoxide) was prepared by the reduction of 2:4-dinitrophenol with potassium cyanide in aqueous solution; in alcoholic solution, considerable quantity of potassium 2:4-dinitro-3-cyanophenoxide is formed. The addition of hydrogen cyanide in those reactions is

discussed with reference to Thiele's theory of conjugated double-linking.

Ammonium metapurpurate, prepared by decomposing potassium metapurpurate by phosphoric acid and then adding an ethereal solution of ammonia to the ethereal solution of the liberated metapurpuric acid, is at first a red, amorphous mass, which gradually becomes crystalline. When barium chloride is added to its aqueous solution, *barium metapurpurate* separates in dark red, glistening needles. The free *acid* (4-*nitro*-2-*hydroxylamino*-3-*cyanophenol*), prepared by cooling ammonium metapurpurate in aqueous solution to 0° and adding the calculated amount of phosphoric acid, is a dark red powder, which decomposes at 92° with evolution of nitric oxide. When quite dry, it is stable; it is decomposed by moisture, although it may be preserved unchanged for days in presence of an excess of water; its ethereal is much more stable than its aqueous solution.

Potassium o-*cresolpurpurate* (*potassium* 5-*nitro*-3-*hydroxylamino*-4-*cyano*-2-*hydroxy*-1-*methylbenzene*), prepared from dinitro-*o*-cresol and potassium cyanide in aqueous solution, yields the corresponding *ammonium* salt, from which o-*cresolpurpuric acid* is readily formed; the latter, when absolutely dry, is a stable, dark reddish-violet powder, and decomposes at 180° with evolution of nitric oxide.

The *potassium* salt of *ethyl* 5-*nitro*-3-*hydroxylamino*-4-*cyano*-2-*hydroxybenzoate*, prepared by the action of potassium cyanide on ethyl dinitrosalicylate, crystallises from water in brick-red needles; the corresponding *ammonium* salt was also prepared. *Ethyl* 5-*nitro*-3-*hydroxylamino*-4-*cyano*-2-*hydroxybenzoate*, prepared by decomposing the potassium salt with phosphoric acid, first forms an amorphous, orange-yellow powder, which crystallises from glacial acetic acid in blood-red needles or scales, and melts and begins to decompose at 186°.

A. McK.

Molecular Rearrangement of Aminophenyl Alkyl Carbonates. Julius Stieglitz and Henry T. Upson (*Amer. Chem. J.*, 1904, 31, 458—502).—It has been shown by Ransom (Abstr., 1900, i, 218) that *o*-aminophenyl ethyl carbonate, formed by the reduction of *o*-nitrophenyl ethyl carbonate with tin and hydrochloric acid, undergoes molecular rearrangement with formation of hydroxyphenylurethane. The present investigation was undertaken with the object of ascertaining the degree to which the tendency to suffer rearrangement exists in the substitution products of *o*-aminophenyl ethyl carbonate and the extent to which the amines or their salts can be isolated as intermediate products, and also to determine the velocity with which the rearrangement takes place and the factors on which it depends.

The results show that each of the *o*-aminophenyl carbonates studied exhibits a tendency to change into its corresponding urethane, and in every case the hydrochloride of an amine can be isolated. A detailed account of this portion of the work is reserved for a future paper.

The following affinity constants, *K aff.*, and velocity constants of rearrangement, *k*, were found by determining the conductivity of

solutions of the hydrochlorides at 0°, according to Stieglitz and Derby's method (this vol., ii, 464).

	K.	K *aff.* $\times 10^{14}$.	k.
4-Aminophenyl methyl carbonate.......... ..	23200	27800	—
4-Aminophenyl ethyl carbonate	22050	26500	—
2-Aminophenyl methyl carbonate............	1040	1250	0·1017
2-Aminophenyl ethyl carbonate	800	960	0·0578
2-Amino-4-methylphenyl ethyl carbonate ..	1020	1225	0·0186
2-Amino-5-methylphenyl ethyl carbonate...	1800	2160	0 0717
2-Amino-6-methylphenyl ethyl carbonate...	880	1050	0·0659

(K signifies that the affinity constant of the base is $K \times$ the degree of dissociation of water, $1 \cdot 2 \times 10^{-14}$; K *aff.* $= K \times 1 \cdot 2 \times 10^{-14}$.)

These results lead to the following conclusions: the *o*-aminophenyl alkyl carbonates are very much weaker bases than the corresponding para-derivatives. 2-Amino-5-methylphenyl ethyl carbonate, containing the methyl group in the *p*-position to the amino-group, is decidedly stronger than the isomeric bases in which the methyl group occupies the *m*-position to the amino-group. The velocity constants indicate that the rearrangement depends entirely on the presence of the free base in solution, that the free acid retards the rearrangement by forming the salt, and that the actual rate of the change is the result of two simultaneous reactions, one a non-reversible reaction of rearrangement of the free base, and the other a reversible reaction which results in a condition of equilibrium between the salt, water, the free acid, and the free base. The velocity constants appear to depend mainly on changes affecting the substituted carboxyl group, and but little on the more or less positive nature of the amino-group; the base containing the methyl-substituted carboxyl group undergoes rearrangement nearly twice as rapidly as the corresponding base containing the ethyl group. The velocity constant is considerably reduced by the substitution of methyl for hydrogen in the para-position to the carboxyl group.

The behaviour of the hydrochlorides of the following halogen derivatives has been studied.

4-Chloro-2-aminophenyl ethyl carbonate, 6-chloro-2-aminophenyl ethyl carbonate, 4-bromo-2-aminophenyl ethyl carbonate, 6-bromo-2-amino-4-methylphenyl ethyl carbonate, 4-bromo-2-amino-6-methylphenyl ethyl carbonate, 4:6-dichloro-2-aminophenyl ethyl carbonate, and 4-chloro-6-bromo-2-aminophenyl ethyl carbonate. The velocity of rearrangement has been determined in $N/32$ solution at 25° and compared with that of the corresponding unsubstituted compounds. The results obtained lead to the following conclusions. The methyl group in the 4-position retards the rearrangement both at 25° and at 0°, whilst in the 6-position it delays the rearrangement somewhat at 25°, but accelerates it slightly at 0°. A halogen atom in the 6-position causes a considerably increased velocity as compared with its effect in the 4-position. The substitution of a halogen atom for hydrogen in the 4-position in the amino-phenyl or -tolyl alkyl carbonates exerts a retarding effect on the velocity of the change. The rearrangement in the solutions of the salts of the halogen derivatives, as in the case of

the unsubstituted compounds, is found to be wholly dependent on the presence of the free base. E. G.

Nitration of 1-Methoxy-(ethoxy)-3-chloro-(bromo)-6-nitrobenzene. JAN J. BLANKSMA (*Rec. trav. chim.*, 1904, **23**, 119—124. Compare Abstr., 1903, i, 164).—When 1-bromo-3 : 4-dinitrobenzene is treated with sodium methoxide dissolved in methyl alcohol, there is formed 3-*bromo*-6-*nitroanisole*, which separates from alcohol in silky needles, melts at 90°, and, with sodium methoxide in methyl alcohol, furnishes the dimethyl ether of 4-nitroresorcinol (Meldola, *Proc.*, 1901, **17**, 131). When the bromonitroanisole is warmed with nitric acid of sp. gr. 1·52, there is formed 3-*bromo*-4 : 6-*dinitroanisole*, which crystallises in colourless spangles, melts at 110°, and is converted by sodium methoxide into the dimethyl ether of 4 : 6-dinitroresorcinol (Meldola, *loc. cit.*). The bromine atom in the bromodinitroanisole is mobile, and the substance furnishes, with ammonia in alcohol, the corresponding dinitroanisidine, which melts at 156°, and with methylamine the corresponding *dinitromethylaminoanisole*, a yellow, crystalline substance which melts at 198°. The analogous *ethylamine* derivative melts at 148° and the 4 : 6-*dinitro*-3-*anilinoanisole* occurs in yellow crystals and melts at 168°.

With nitric acid of sp. gr. 1·52, bromodinitroanisole furnishes 3-bromo-2 : 4 : 6-trinitroanisole, which reacts with amines like the corresponding chloro-derivative (Abstr., 1903, i, 158).

When 3-chloro-6-nitroanisole, prepared like the analogous bromo-derivative, is warmed with nitric acid of sp. gr. 1·52, 3-*chloro*-4 : 6-*dinitroanisole* is formed; this crystallises in colourless needles or spangles and melts at 105°. With sodium sulphide dissolved in alcohol, it is converted into *tetranitrodimethoxydiphenyl sulphide*, which forms yellow crystals melting at 204°, and with sodium disulphide into the corresponding *disulphide*, which melts and decomposes at 236°.

3-*Chloro*-4 : 6-*dinitrophenyl ethyl ether*, prepared like its lower homologue, melts at 112° and, with aniline dissolved in alcohol, furnishes 4 : 6-*dinitro*-3-*anilinophenyl ethyl ether*, which forms yellow crystals and melts at 170°.

These observations indicate that in the nitration of these substances, derivatives having the nitro-group in the para-position relatively to the alkyloxy-group are principally formed, the amount of ortho-derivative produced, if any, being very small. T. A. H.

Anethole. PAUL HOERING (*Ber.*, 1904, **37**, 1542—1560. Compare Hell, Abstr., 1895, i, 341; 1896, i, 169; with Gärthner, Abstr., 1895, i, 341; with von Günthert, Abstr., 1896, i, 20; with Hollenberg, Abstr., 1896, i, 354).—Attempts to convert 3-bromo-4-methoxy-1-β-bromopropionylbenzene into the corresponding alcohol,

$$OMe\cdot C_6H_3Br\cdot CO\cdot CHMe\cdot OH,$$

by the action of aqueous or alcoholic potassium hydroxide or barium hydroxide gave only bromoanisic acid (compare Breuninger, Diss., Erlangen); boiling alcoholic potassium acetate, on the other hand, converts the ketone into the *acetyl* derivative,

$$OMe\cdot C_6H_3Br\cdot CO\cdot CHMeAc,$$

which crystallises from alcohol in colourless needles and melts at 87°; the analogous *benzoyl* derivative, $OMe·C_6H_3Br·CO·CHMeBz$, melts at 116°. On nitration, 3-bromo-4-methoxy-1-β-bromopropionylbenzene gives a *nitro*-derivative, $C_{10}H_9O_4NBr_2$, which crystallises from light petroleum in stellate aggregates of yellow, prismatic needles and melts at 92°.

On dissolving bromoanethole dibromide in concentrated nitric acid, 3 : 5-dibromo-4-methoxy-1-β-bromopropionylbenzene,

$$OMe·C_6H_2Br_2·CO·CHMeBr$$

(*infra*) is obtained, which, on oxidation with chromic acid, affords 3 : 5-dibromoanisic acid. By fuming nitric acid of sp. gr. 1·52, on the other hand, bromoanethole dibromide is converted into 2 : 6-dibromo-4-nitroanisole.

3 : 5-Dibromoanethole dibromide is best prepared by adding anethole to a slight excess of bromine in a reflux apparatus; it crystallises from light petroleum and melts at 101·5°. With nitric acid of sp. gr. 1·48 it gives rise to 3 : 5-dibromo-4-methoxy-1-β-propionylbenzene, and, on oxidation with dilute nitric acid, it gives 3 : 5-dibromoanisic acid; 2 : 6-dibromo-4-nitroanisole is formed by the action of fuming nitric acid (sp. gr. 1·52). Boiling absolute methyl or ethyl alcohol do not attack dibromoanethole dibromide; boiling alcoholic sodium ethoxide, however, rapidly converts it into 3 : 5-*dibromo*-4-*methoxy*-1-β-*bromopropylenebenzene*, $OMe·C_6H_2Br_2·CH\!:\!CMeBr$, which crystallises from light petroleum, melts at 58°, and combines readily with bromine to form 3 : 5-*dibromo*-4-*methoxy*-1-αββ-*tribromopropylbenzene*,

$$OMe·C_6H_2Br_2·CHBr·CMeBr_2,$$

melting at 92°.

3 : 5-Dibromo-4-methoxy-1-β-bromopropylenebenzene is transformed by atmospheric oxygen in presence of traces of hydrogen bromide into the *ketone*, $OMe·C_6H_2Br_2·CO·CHMeBr$, which crystallises from alcohol or light petroleum in slender needles and melts at 101°; the ketone is remarkable for emitting during recrystallisation luminous radiations which affect a photographic plate, but are not able to discharge an electroscope (compare Armstrong and Lowry, this vol., ii, 5). On oxidation with chromic acid in acetic acid solution, 3 : 5-dibromo-4-methoxy-1-β-bromopropylenebenzene gives 3 : 5-dibromoanisic acid; by alcoholic sodium ethoxide, the olefine is not affected.

In the bromination of anethole with an excess of bromine, a ψ-p-*dibromopropyldibromophenol*, $C_9H_8OBr_4$, is always produced in varying proportions; it melts at 112—113° and seems to be formed from dibromoanethole dibromide by the elimination of the methyl group, as it can be obtained from this substance by heating it with hydrobromic acid for 3 hours at 120°. It has all the properties of a pseudo-bromide (Zincke, Auwers), and with lead acetate in glacial acetic acid gives at 70° an *acetyl* derivative, $C_{11}H_{11}O_3Br_3$, which crystallises from alcohol in large, six-sided plates and melts at 107—108°.

The author points out that whilst bromoanethole dibromide is converted by sodium ethoxide, even more readily than anethole dibromide, into a ketone, through the stages $R·CHBr·CHMeBr \longrightarrow R·CH(OMe)·CHMeBr \longrightarrow R·C(OMe)\!:\!CHMe \longrightarrow R·C(OH)\!:\!CHMe \longrightarrow$

$R \cdot CO \cdot CH_2Me$, dibromoanethole dibromide is at once transformed into 3 : 5-dibromo-4-methoxy-1-β-bromopropylenebenzene. In order to explain this anomalous behaviour on the part of the dibromo-derivative, the author assumes that anethole dibromide and bromoanethole dibromide are capable of existing in isodynamic forms, for example :

$$\text{I. } OMe \cdot C \lessdot \begin{matrix} CH \cdot CH \\ CH{:}CH \end{matrix} \gtrdot C \cdot CHBr \cdot CHMeBr \text{ and}$$

$$\text{II. } OMe \cdot C \lessdot \begin{matrix} CH \cdot CHBr \\ CH = CH \end{matrix} \gtrdot C{:}CH \cdot CHMeBr,$$

the second of which enters into action with the alkali to give the primary methoxy-derivative, which later decomposes to form the ketone. In favour of this view are the facts that anethole and bromoanethole dibromides often solidify with difficulty, and that they readily give rise to ketones containing bromine in the benzene nucleus. Dibromoanethole dibromide, on the other hand, interacts only as if it had the structure I. W. A. D.

Dinitrophenyl Ethers of 3-Chloro-4-aminophenol and of *p*-Aminophenol. FRÉDÉRIC REVERDIN and AUGUST DRESEL (*Ber.*, 1904, 37, 1516—1519).—3-*Chloro*-2′ : 4′-*dinitro*-4-*aminophenyl ether*, $NH_2 \cdot C_6H_3Cl \cdot O \cdot C_6H_3(NO_2)_2$, prepared by boiling an alcoholic solution of 1-chloro-2 : 4-dinitrobenzene and 3-chloro-4-aminophenol with an excess of sodium acetate for several hours, crystallises in long, brownish-yellow needles and melts at 137°. If the alcoholic mixture is heated in absence of sodium acetate, 2-chloro-2′ : 4′-dinitro-4-hydroxydiphenylamine is the sole product. When, however, 2-chloro-4-aminophenol is heated with 1-chloro-2 : 4-dinitrobenzene, either with or without the addition of sodium acetate, the principal product is always 3-chlorodinitro-4-hydroxydiphenylamine (Abstr., 1903, i, 857). The position of the chlorine atom in the nucleus thus exercises a great influence on the course of the interaction. On attempting to chlorinate 3-chloro-2′ : 4′-dinitro-4-aminophenyl ether with sodium chlorate and hydrochloric acid, a fission of the molecule occurs, trichloroquinone being produced.

The ether is easily diazotised, and the diazo-salt formed may be coupled with phenols to form dyes, but the products are not sufficiently resistant to alkalis to be of practical value. Satisfactory dyes, however, are obtained from the diazo-salts of 2′ : 4′-*dinitro*-4-*aminophenyl ether*, $NH_2 \cdot C_6H_4 \cdot O \cdot C_6H_3(NO_2)_2$, which is obtained in the form of its *acetyl* derivative by heating an alcoholic mixture of *p*-acetylaminophenol, 1-chloro-2 : 4-dinitrobenzene, and potassium hydroxide for 2 hours ; the *acetyl* compound crystallises from benzene in lustrous, yellowish-white leaflets melting at 195°, and the *base* from alcohol in dark yellow leaflets melting at 144°. In presence of sodium acetate, the base combines with 1-chloro-2 : 4-dinitrobenzene to form the diphenylamine derivative, $C_6H_3(NO_2)_2 \cdot O \cdot C_6H_4 \cdot NH \cdot C_6H_3(NO_2)_2$, melting at 225° (D.R.-P., 1899, 111892). W. A. D.

3-Amino-6-hydroxytoluene-ω-sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 150313).—Sulphites react with 3-nitro-6-hydroxybenzyl chloride to form 3-*nitro*-6-*hydroxytoluene*-ω-

sulphonic acid, which is reduced by zinc dust and acid to 3-*amino*-6-*hydroxytoluene-ω-sulphonic acid*, forming colourless needles, stable in the air, dissolving sparingly in water, readily in alkalis, and charring without melting. It is not decomposed by boiling with alkali hydroxides. The acid finds application as a photographic developer.

C. H. D.

3-Chloro-4 : 6-dinitrotoluene and 3-Chloro-2 : 4 : 6-trinitrotoluene. FRÉDÉRIC REVERDIN, AUGUSTE DRESEL, and ERNEST DELÉTRA (*Bull. Soc. chim.*, 1904, [iii], 31, 631—635. Compare Abstr., 1900, i, 638).—The *acetyl* derivative of the 4′-hydroxyphenyl-4 : 6-dinitro-*m*-tolylamine already described (*loc. cit.*) crystallises from acetone in long, transparent needles or from benzene in reddish-brown leaflets, melts at 146—147°, and, when treated with sodium chlorate and hydrochloric acid, furnishes 4′-*acetoxyphenyl*-2-*chloro*-4 : 6-*dinitro*-3-*tolylamine*, which melts at 128°. When the hydroxy-compound itself is chlorinated, dichloro-derivatives analogous to those produced with dinitrohydroxydiphenylamine are formed (compare Abstr., 1903, i, 857).

When 3-chloro-4 : 6-dinitrotoluene dissolved in alcohol is condensed with 2-chloro-4-aminophenol in presence of sodium acetate, there is produced 3′-*chloro*-4′-*hydroxyphenyl*-4 : 6-*dinitro*-m-*tolylamine*, which forms reddish-yellow, prismatic needles and melts at 176°.

3′ : 5′-*Dichloro*-4′-*hydroxyphenyl*-4 : 6-*dinitro*-3-*tolylamine*, similarly prepared from the corresponding dichloroaminophenol, forms prismatic leaflets of a yellowish-green tint and melts at 230°. With anisidine, the corresponding 4′-*methoxyphenyl*-4 : 6-*dinitro*-m-*tolylamine* is formed; this separates from a mixture of alcohol and acetone in brilliant, brick-red prisms, and from alcohol in golden-yellow needles, which pass into the red variety immediately on warming or slowly when kept; it melts at 139°. 4′-*Aminophenyl*-4 : 6-*dinitro*-3-*tolylamine*, similarly prepared from *p*-phenylenediamine, crystallises from dilute acetone in purple-red prisms and melts at 166°.

When the chlorodinitrotoluene is nitrated at 150—175° or when chlorotoluene is treated with sulphuric (66° B.) and nitric acids (49·4° B.) at 160°, 3-*chloro*-2 : 4 : 6-*trinitrotoluene* is formed; this crystallises from acetic acid in long, colourless needles, and from dilute acetone in spangles, melts at 148·5°, and is readily soluble in the usual solvents. Its solution in alcohol gives, like the chlorodinitrotoluene, a blue coloration passing rapidly into brownish-yellow with solutions of ammonia or sodium hydroxide. When warmed with ammonia in alcohol, it furnishes 2 : 4 : 6-trinitro-*m*-toluidine (Abstr., 1883, 59). With aniline, there is produced *phenyl*-2 : 4 : 6-*trinitro*-m-*tolylamine*, which crystallises from dilute acetone in golden leaflets, melts at 150°, and is soluble in chloroform, less so in ether, and slightly so in light petroleum. The *corresponding* derivative prepared from *p*-toluidine forms yellowish-red needles from acetic acid or dilute acetone and melts at 127°. With *p*-aminophenol, 4′-*hydroxyphenyl*-2 : 4 : 6-*trinitro*-m-*tolylamine* is formed; this crystallises from alcohol in brown scales and melts at 207°.

4′-*Aminophenyl*-2 : 4 : 6-*trinitro*-m-*tolylamine*, similarly obtained

from *p*-phenylenediamine, crystallises from dilute acetone in reddish-tinted spangles, melts at 198·5°, and is readily soluble in acetone and acetic acid, and slightly so in light petroleum and water. T. A. H.

Condensation of β-Naphthol with Formaldehyde and Ammonia. MARIO BETTI (*Gazzetta*, 1904, 34, i, 212—223. Compare Abstr., 1901, i, 81, 611, 703; 1903, i, 510).—Formaldehyde differs from other aldehydes in its action on β-naphthol and an amine, with which it yields tertiary tri-β-naphtholmethyleneamine bases.

Tri-β-naphtholmethyleneamine, $N(CH_2\cdot C_{10}H_6\cdot OH)_3$, obtained by the interaction of β-naphthol, formaldehyde, and alcoholic ammonia, crystallises from ethyl acetate in long, massive needles melting at 164°. It is accompanied by a yellow *substance* melting at 197°, and yielding with ethyl acetate a solution exhibiting a strong, greenish-yellow fluorescence, and by a *compound*,

$$2N(CH_2\cdot C_{10}H_6\cdot OH)_3,6CH_2O,H_2O,$$

which is deposited in massive, rhombohedral crystals melting at about 158°; the latter substance, when boiled in ethyl acetate solution, passes readily into tri-β-naphtholmethyleneamine. The *acetate* of the latter, $N(CH_4\cdot C_{10}H_6\cdot OH)_3,CH_3\cdot CO_2H$, separates from alcohol in minute, almost white plates melting at 190—191°. The *hydrochloride* separates from alcohol in shining laminæ which melt and decompose at about 220° and yield the base when treated with potassium hydroxide; the *benzoyl chloride* derivative, $N(CH_2\cdot C_{10}H_6\cdot OH)_3,HCl,BzCl$, crystallises from acetic acid in pale rose-coloured, stout rhombohedra, which melt and decompose at about 210°. T. H. P.

Distillation of Guaiacol with Lead Oxide. ROBERT PSCHORR and M. SILBERBACH (*Ber.*, 1904, 37, 2149—2152).—When distilled with lead oxide, guaiacol is converted into veratrole, the lead salt of guaiacol being first formed and methylated at the expense of the methyl radicle in a second molecule of guaiacol. The lead and sodium derivatives of guaiacol also give veratrole when distilled. Similarly, the lead derivative of ethyl vanilinate forms veratric acid, whilst the lead derivative of resorcinol monomethyl ether yields resorcinol dimethyl ether on distillation. E. F. A.

New Reducing Agent for the Preparation of Thiophenol. W. P. WINTER (*Amer. Chem. J.*, 1904, 31, 572—577).—The method usually adopted for the preparation of thiophenol is that described by Otto (Abstr., 1877, ii, 749), which consists of the reduction of benzenesulphonic chloride by means of zinc dust; this process, however, gives only about two-thirds of the theoretical yield. It is found that if the reduction is effected by the action of stannous chloride in the presence of a small quantity of zinc dust, a quantitative yield can be obtained. E. G.

o-Aminobenzyl Alcohol and μ-Methylphenopentoxazole. [3-Methyl-2:4-benzoxazine.] KARL AUWERS (*Ber.*, 1904, 37, 2249—2267).—*o-Benzoylaminobenzyl alcohol*, $NHBz\cdot C_6H_4\cdot CH_2\cdot OH$, formed by the action of benzoyl chloride and potassium hydrogen carbonate on

o-aminobenzyl alcohol in ethereal solution, crystallises in long, delicate, white needles and melts at 132—133° (compare Paal and Bodewig, Abstr., 1893, i, 20).

o-Aminobenzyl acetate, $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot OAc$ (Söderbaum and Widman, Abstr., 1889, 972; Gabriel and Posner, Abstr., 1895, i, 191), is formed by reduction of *o*-nitrobenzyl acetate with aluminium amalgam in ethereal solution. It is a colourless oil having an odour of aniline; the *picrate* melts at 105°. The anhydrous salts are stable towards mineral acids, but in aqueous solution are rapidly hydrolysed with formation of *o*-aminobenzyl alcohol. When warmed in ethereal solution, *o*-aminobenzyl acetate is slowly converted into *o*-acetylaminobenzyl alcohol, $NHAc \cdot C_6H_4 \cdot CH_2 \cdot OH$, which melts at 115—116°.

With hydrogen chloride in an anhydrous solution, *o*-acetylaminobenzyl alcohol forms an *additive* compound, $C_9H_{12}O_2NCl$, which is obtained in glistening, delicate needles and melts at 120—125°. With alkalis, it does not regenerate *o*-acetylaminobenzyl alcohol, but yields 3-methyl-2 : 4-benzoxazine (μ-methylphenopentoxazole; Gabriel and Posner, *loc. cit.*). The picrate and the platinichloride of 3-methyl-2 : 4-benzoxazine can be obtained directly from the additive compound. The *platinichloride* is salmon-coloured and melts and decomposes at 219°. The *hydrochloride* is rapidly converted by water into the hydrochloride of *o*-aminobenzyl acetate.

The action of hydrochloric acid on acetylaminobenzyl alcohol in presence of moisture or of hydrogen chloride on the dry acetate over sulphuric acid leads to the formation chiefly of the hydrochloride of *o*-aminobenzyl acetate. G. Y.

Reduction of Triphenylcarbinol. JOSEF HERZIG (*Ber.*, 1904, 37, 2107).—The reduction of triphenylcarbinol to triphenylmethane is described by Acree (this vol., i, 315), who omits to mention that this reduction had already been effected by Herzig and Wengraf (Abstr., 1901, i, 702). A. McK.

Lupeol. ERNST SCHULZE (*Zeit. physiol. Chem.*, 1904, 41, 474—476. Compare Likiernik, Abstr., 1891, 551 and 1446).—Lupeol from *Lupinus albus* appears to be identical with that from *L. luteus.*

Lupeol itself melts after several crystallisations at 211—212°, its benzoate at 265—266°, and its acetate at 141—142°. J. J. S.

Ethyl Diazoacetate and Systems with Conjugated Double Linkings. CARL VON DER HEIDE (*Ber.*, 1904, 37, 2101—2106).—According to Thiele, in a conjugated system of contiguous double linkings, two univalent substituents take up the 1 : 4-position. To test how bivalent radicles behave in a similar case, the author has studied the action of ethyl diazoacetate on phenylbutadiene. The addition does not take place in the $\alpha\delta$-position in the phenylbutadiene molecule, since a *cyclo*pentene derivative is not produced. On the other hand, a trimethylene derivative of the type

$$CHPh{:}CH \cdot CH<\begin{matrix} CH_2 \\ | \\ CH \cdot CO_2R \end{matrix}$$

is formed. The phenyl group thus prevents the formation of a tri-

methylene ring at the contiguous $\alpha\beta$-double linking, so that the addition of the $(CH\cdot CO_2R)<$ group at the end of the side-chain, accompanied by the closing of the ring, takes place with greater ease.

Phenylbutadiene was prepared by the action of magnesium methyl bromide on cinnamaldehyde (compare Klages, Abstr., 1902, i, 669); it was found convenient to decompose the crude product resulting from the Grignard reaction by sulphuric acid instead of by water, as directed by Klages. When phenylbutadiene (1 mol.) and ethyl diazoacetate (1 mol.) were heated for 30 hours at 70—90°, nitrogen was evolved and *ethyl* 1-*styryl*cyclo*propane-2-carboxylate*,

$$CHPh{:}CH\cdot CH<\begin{matrix}CH_2\\|\\CH\cdot CO_2Et\end{matrix},$$

was formed; it melts at 42—43° and decolorises alkaline permanganate.

1-*Styryl*cyclo*propane-2-carboxylic acid*, prepared by hydrolysis of the preceding ester, separates in colourless leaflets, of a mother-of-pearl lustre, or in prisms and melts at 130°. Its *amide* melts at 160°. Its *dibromide* forms glistening, white crystals and melts at 203—204°; it does not decolorise alkaline permanganate.

The constitution of 1-styryl*cyclo*propane-2-carboxylic acid is proved by its yielding, on oxidation, a mixture of benzoic acid and *trans-cyclo*propane-1 : 2-dicarboxylic acid. When 1-styryl*cyclo*propane-2-carboxylic acid was reduced by sodium in amyl alcohol solution, an acid was obtained, the amide of which melted at 95—96°; this acid is formed by the disruption of the trimethylene ring, and is either ϵ-phenylhexoic or δ-phenyl-β-methylvaleric acid. Conditions are quoted where normal reduction by sodium amalgam takes place without disruption of the trimethylene ring; the *amide* of 1-β-*phenylethyl*-cyclo*propane-2-carboxylic acid* forms glistening leaflets and melts at 104—105°.

A. McK.

m-Aminobenzonitrile and some of its Derivatives. MARSTON T. BOGERT and HAL T. BEANS (*J. Amer. Chem. Soc.*, 1904, 26, 464—499. Compare Bogert and Hand, Abstr., 1903, i, 292).—*m*-Aminobenzonitrile may be prepared from *m*-nitroaniline by the Sandmeyer reaction or from benzonitrile by nitration and subsequent reduction of *m*-nitrobenzonitrile. m-*Nitrobenzonitrile* forms silky needles and melts at 117—117·5° (corr.). m-*Aminobenzonitrile* separates from ether in hexagonal prisms and from carbon tetrachloride in silky needles, which melt at 53—53·5° (corr.). Its *hydrochloride* crystallises from alcohol in pearly flakes. *iso*Phthalonitrile, $C_6H_4(CN)_2$, separates from a mixture of ethyl acetate and light petroleum in needles and melts at 161·5—162° (corr.).

m-*Formylaminobenzonitrile*, $CN\cdot C_6H_4\cdot NH\cdot COH$, prepared from *m*-aminobenzonitrile and formic acid, separates from water in microscopic needles and melts at 150·5—151° (corr.). m-*Acetylaminobenzonitrile*, $CN\cdot C_6H_4\cdot NHAc$, obtained from *m*-aminobenzonitrile and acetic anhydride, separates from water in slender needles and melts at 130·5—131° (corr.). m-*Propionylaminobenzonitrile*, prepared from

m-aminobenzonitrile and propionic anhydride, separates from a mixture of benzene and light petroleum in needles and melts at 83·5—84° (corr.). n-*Butyryl*-m-*aminobenzonitrile* separates from a mixture of benzene and light petroleum and melts at 72·5—73·5° (corr.). iso*Butyryl*-m-*aminobenzonitrile* separates from dilute alcohol in pearly flakes and melts at 101° (corr.). iso*Valeryl*-m-*aminobenzonitrile* separates from a mixture of benzene and light petroleum in pearly flakes and melts at 77—78° (corr.). In those acyl compounds, accordingly, the melting point decreases with increase of carbon atoms in the aliphatic chain.

m-*Acetylaminobenzamide*, $NHAc \cdot C_6H_4 \cdot CO \cdot NH_2$, prepared by hydrolysing *m*-acetylaminobenzonitrile with alkaline hydrogen peroxide, crystallises from water in fine needles and melts at 216—216·5° (corr.).

m-*Benzoylaminobenzonitrile* separates from dilute alcohol in pearly flakes and melts at 141·5—142° (corr.). 3-*Nitrobenzoyl*-m-*aminobenzonitrile*, best prepared by dissolving the *m*-aminobenzonitrile in pyridine and then adding a pyridine solution of *m*-nitrobenzoyl chloride, crystallises from alcohol in needles and melts at 196·5—197° (corr.). 4-*Nitrobenzoyl*-m-*aminobenzonitrile* separates from alcohol in yellow needles and melts at 250—251° (corr.). *Benzenesulphonyl*-m-*aminobenzonitrile* separates from aqueous alcohol in silky needles and melts at 126·5—127° (corr.).

m-*Cyanophenylurethane*, $CN \cdot C_6H_4 \cdot NH \cdot CO_2Et$, prepared from *m*-aminobenzonitrile and ethyl chlorocarbonate, forms prismatic crystals and melts at 61—62° (corr.); when digested with hydrogen peroxide and sodium hydroxide, it forms *m*-urethanebenzamide, $NH_2 \cdot CO \cdot C_6H_4 \cdot NH \cdot CO_2Et$, which crystallises in flakes and melts at 159—160°. m-*Cyanophenylcarbamide*, $CN \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, prepared from *m*-aminobenzonitrile hydrochloride and potassium cyanate, separates from a mixture of ethyl acetate and light petroleum in needles and melts at 160—162° (corr.). m-*Cyanocarbanilide*,

$$CN \cdot C_6H_4 \cdot NH \cdot CO \cdot NHPh,$$

prepared from *m*-aminobenzonitrile and phenylcarbimide, crystallises from alcohol in needles and melts at 170·5—171° (corr.). When heated at 175°, it forms *di*-m-*cyanocarbanilide*, $CO(NH \cdot C_6H_4 \cdot CN)_2$, which separates from alcohol in needles and melts at 199°. This may also be prepared from *m*-aminobenzonitrile and *m*-cyanophenylcarbamide or from *m*-aminobenzonitrile and carbonyl chloride. m-*Cyanothiocarbanilide*, $CN \cdot C_6H_4 \cdot NH \cdot CS \cdot NHPh$, prepared from *m*-aminobenzonitrile and phenylcarbimide, separates from chloroform in yellow, rhombic crystals and melts at 143—144° (corr.).

Ethyl m-*cyano-oxanilate*, $CN \cdot C_6H_4 \cdot NH \cdot CO \cdot CO_2Et$, obtained from *m*-aminobenzonitrile and ethyl oxalate, crystallises from alcohol in needles and melts at 148—148·5° (corr.); when heated above its melting point, it decomposes into ethyl oxalate and oxaldi-*m*-cyanoanilide. m-*Cyanophenyloxamide*, $CN \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, prepared by the action of ammonia on ethyl *m*-cyano-oxanilate, separates from alcohol in pearly flakes and melts at 245—246° (corr.). *Oxalyl*-m-*cyanoanilide*, $CN \cdot C_6H_4 \cdot NH \cdot CO \cdot CO \cdot NHPh$, prepared by heating ethyl *m*-cyano-

oxanilate with aniline, crystallises from alcohol in silky needles and melts at 205—206° (corr.). *Oxalyl*-m-*cyanoanilide*,

$$C_2O_2(NH \cdot C_6H_4 \cdot CN)_2,$$

prepared by melting ethyl *m*-cyano-oxanilate (1 mol.) with *m*-aminobenzonitrile (1 mol.) in presence of anhydrous zinc chloride, crystallises from amyl alcohol and does not melt at 300°.

m-*Cyanosuccinanilic acid*, $CN \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$, prepared from succinic anhydride and *m*-aminobenzonitrile, crystallises in silky flakes and melts at 132—133° (corr.); its *silver* and *calcium* salts were prepared, the latter crystallising with $4H_2O$. Its *methyl ester* crystallises from dilute methyl alcohol in slender needles and melts at 88—89° (corr.). Its *ethyl ester* separates from a mixture of benzene and light petroleum in needles and melts at 84—84·5° (corr.). Its *amide*, prepared by the action of ammonia on its methyl or ethyl ester, crystallises from water in glistening plates and melts at 184° (corr.) if heated quickly. Its *acid chloride*, prepared by the action of phosphorus pentachloride, separates from chloroform in shining needles and melts at 80° (corr.). m-*Cyanosuccinanil*, $CN \cdot C_6H_4 \cdot N \langle {CO \cdot CH_2 \atop CO \cdot CH_2}$, prepared by the action of acetic anhydride on *m*-cyanosuccinanilic acid, crystallises in needles and melts at 137—137·5° (corr.). By the action of alkaline hydrogen peroxide, it is converted into m-*carbaminsuccinanilic acid*, $NH_2 \cdot CO \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which crystallises in needles and melts at 203—205° (corr.).

Condensation products of aromatic amines with chloral have been investigated by Wallach, Eibner, Wheeler, and others. Condensation products of *m*-aminobenzonitrile and chloral are described.

Trichlorohydroxyethyl-m-*cyanophenylamine*,

$$CN \cdot C_6H_4 \cdot NH \cdot CH(OH) \cdot CCl_3,$$

forms prismatic crystals and melts and decomposes at 102—103° (corr.) to form *trichloroethyldi*-m-*cyanophenylamine*,

$$CCl_3 \cdot CH(NH \cdot C_6H_4 \cdot CN)_2,$$

which is best prepared by the action of anhydrous chloral on *m*-aminobenzonitrile in toluene solution; it separates from aqueous alcohol in needles or in feathery plates and melts at 165—167° (corr.) when quickly heated. *Tribromoethyldi*-m-*cyanophenylamine* chars to a black tar at about 130°.

Tribromo-m-*aminobenzonitrile*, prepared by brominating *m*-aminobenzonitrile in glacial acetic acid solution, crystallises from alcohol in needles and melts at 177—178°. A. McK.

New Derivatives of Salol. Attilio Purgotti and N. Monti (*Gazzetta*, 1904, **34**, i, 267—278).—*Benzoylsalicylic acid*,

$$CO_2Ph \cdot C_6H_4 \cdot OBz,$$

prepared by the action of benzoyl chloride on salol in presence of sodium hydroxide, crystallises from alcohol in shining needles, which melt at 80·5—81°, have no taste or smell, and dissolve slightly in the ordinary solvents. With ferric chloride, it gives the phenol reaction. On hydrolysis with alcoholic potassium hydroxide, it yields benzoic and

salicylic acids. Increasing doses, starting from 0·1 gram, of benzoyl salol were administered to two rabbits weighing 2·30 and 2·24 kilos. respectively, but the only effect produced, even with the largest doses, was a diminution in appetite.

Benzoylsalicylanilide, $NHPh\cdot CO\cdot C_6H_4\cdot OBz$, obtained together with phenol by the action of aniline (1 mol.) on benzoylsalol (1 mol.), separates from alcohol in colourless, acicular crystals melting at 180°.

Benzoylsalicyl-o-toluidide, $C_6H_4Me\cdot NH\cdot CO\cdot C_6H_4\cdot OBz$, prepared from benzoylsalol and *o*-toluidine, is deposited from alcohol in shining crystals melting at 136°.

3-*Bromo*-5-*nitrosalicylic acid*,

$$CO_2Ph\cdot C_6H_2Br(NO_2)\cdot OH\ [CO_2Ph : OH : Br : NO_2 = 1 : 2 : 3 : 5],$$

prepared by the action of concentrated nitric acid (about 2 mols.) on an acetic acid solution of dibromosalol (1 mol.), separates from acetic acid in shining, colourless crystals melting at 165°.

3-*Bromo*-5-*nitrosalicylanilide*, $NHPh\cdot CO\cdot C_6H_2Br(NO_2)\cdot OH$, prepared from the preceding compound and aniline, is deposited from alcohol in pale yellow crystals melting at 221°.

3-*Bromo*-5-*nitrosalicyl*-p-*toluidide*,

$$C_6H_4Me\cdot NH\cdot CO\cdot C_6H_2Br(NO_2)\cdot OH,$$

forms shining, golden-yellow needles, which blacken at 230° and melt at 256°.

3-*Bromo*-5-*nitrosalicylphenylhydrazide*,

$$NHPh\cdot NH\cdot CO\cdot C_6H_2Br(NO_2)\cdot OH,$$

crystallises from alcohol in shining, yellow scales melting at 190°; it reduces Fehling's solution in the cold and does not combine with aldehydes or ketones.

3-Bromo-5-nitrosalicylic acid also reacts readily with *o*-toluidine, yielding a *product* melting at about 250°. With α- and β-naphthylamines it reacts with difficulty, and with diphenylamine not at all.

T. H. P.

Bromo-derivatives of Indigotin. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 149899, 149940, and 149983. Compare Abstr., 1903, i, 345; this vol., i, 57, 167).—Pyridine dibromide, prepared by the addition of bromine to a solution of pyridine hydrochloride, reacts with indigotin at 90—100°, forming bromoindigotin and pyridine hydrobromide, the latter being recovered. Starch bromide also gives up its bromine to indigotin when intimately mixed with it, forming bromo- and dibromo-indigotin. The starch is converted into soluble starch and may be removed by boiling with water. Methylindigotin yields a blue monobromo- and a bluish-green dibromo-derivative.

Bromo-derivatives of indigotin may also be prepared by electrolysing solutions of bromides, in which indigotin or indigo-white is suspended. No diaphragm is necessary, as hydrogen has no action on the products. The method has the advantage that small quantities of bromine are always in presence of an excess of indigotin. The products closely resemble those obtained by dry bromination, but it has not yet been determined whether they are identical with them or with the products prepared synthetically from indoxyl.

C. H. D.

*cyclo*Gallipharic Acid. HERMANN KUNZ-KRAUZE and PAUL SCHELLE (*J. pr. Chem.*, 1904, [ii], 69, 385—386, 387—432. Compare Knoevenagel, Abstr., 1896, i, 210).—After removal of gallic acid, ellagic acid, &c., from the residue of the ethereal extract obtained in the technical preparation of tannin from gall nuts there remains a green mass, from which *cyclo*gallipharic acid is obtained by extraction with glacial acetic acid.

cyclo*Gallipharic acid*, $OH\cdot C_{20}H_{34}\cdot CO_2H$, crystallises from alcohol in sheaves of prisms, melts at 89°, and when heated above 200° evolves an aromatic, combustible gas, and acraldehyde when strongly heated, especially with potassium hydrogen sulphite. The acid is insoluble in water, but soluble in alcohol, ether, chloroform, benzene, carbon disulphide, light petroleum, aqueous alkalis, or ammonia. The silver salt,

$$C_{20}H_{35}O\cdot CO_2Ag,$$

and the calcium salt, $(C_{20}H_{35}O\cdot CO_2)_2Ca$, are described.

The acid dissolves in concentrated sulphuric acid with the formation of a colourless sulphonic acid which is soluble in water. On addition of sulphuric acid, the solution of *cyclo*gallipharic acid in glacial acetic acid slowly assumes a green colour (Liebermann's cholesterol reaction), but in chloroform solution the addition of sulphuric acid produces no coloration.

The *acetyl* derivative, $C_{20}H_{34}(CO_2H)\cdot OAc$, crystallises in long, white prisms, melts at 71°, is soluble in aqueous alkalis, and gives no coloration with ferric chloride in neutral solutions. The *silver* salt,

$$C_{20}H_{34}(OAc)\cdot CO_2Ag,$$

is described.

Attempts to prepare a benzoyl derivative resulted, with the Schotten-Baumann method in a pasty mass, with Einhorn's method in an *additive* compound with pyridine, $C_{21}H_{36}O_3,C_5H_5N$.

The *ethyl* ester, $C_{20}H_{35}O\cdot CO_2Et$, crystallises in long, glistening needles and melts at 37°. With ferric chloride in alcoholic solution, it gives a violet coloration.

*cyclo*Gallipharic acid combines with 1 mol. of iodine; with bromine in aqueous solution it forms the *compound* $C_{21}H_{34}O_3Br_2,HBr$, which crystallises in small prisms, melts at 61°, and gives a violet coloration with ferric chloride. The ethyl ester forms the *bromine* compound, $C_{21}H_{33}O_3Br_2Et$, which melts at 46°.

The action of nitric acid on *cyclo*gallipharic acid leads to the formation of oxalic acid, butyric acid, and two dinitro-compounds. The *α-dinitro*-compound, $C_{15}H_{24}O(NO_2)_2$, crystallises in colourless, prismatic needles, melting at 63·5°; the *β-dinitro*-compound, $C_{15}H_{24}O(NO_2)_2$, crystallises in reddish-yellow leaflets and melts at 59·5°.

Reduction of the dinitro-compounds with zinc dust in aqueous solution, or with "excited" aluminium (Wislicenus, Abstr., 1896, i, 671), leads to the formation of a *nitroamino*-compound, $NO_2\cdot C_{15}H_{23}(NH_2)\cdot OH$, which crystallises with H_2O in green leaflets, melts at 47°, and is very unstable. When heated at 200°, *cyclo*gallipharic acid loses carbon dioxide and yields a *ketoanhydride*, $OH\cdot C_{20}H_{34}\cdot CO\cdot C_{20}H_{34}\cdot OH$, which crystallises in fatty prisms, melts at 48°, is easily soluble to neutral solutions in organic solvents, and gives no coloration or precipitation with ferric chloride or silver nitrate.

When heated at 250°, *cyclo*gallipharic acid yields cyclo*gallipharol*, $C_{20}H_{35}\cdot OH$, or cyclo*gallipharone*, $C_{19}H_{36}\colon CO$, which crystallises in colourless needles, melts at 46°, and forms a *bromo*-derivative, crystallising in needles. It does not form a compound with hydroxylamine (compare Abstr., 1899, i, 200). The same derivative, $C_{20}H_{36}O$, is obtained along with hydrocarbons of the series C_nH_{2n} (heptene—undecene), when calcium *cyclo*gallipharate is distilled; it is also formed along with acetic acid, oxalic acid, and 4-hydroxy-*m*-xylene when *cyclo*gallipharic acid is fused with potassium hydroxide at 300°, or with aqueous potassium hydroxide at 150° under pressure. Oxidation of *cyclo*gallipharic acid with potassium permanganate in alkaline solution leads to the formation of *n*-butyric acid, oxalic acid, glycerol, and gallipharic acid.

Gallipharic acid, $C_{15}H_{31}\cdot CO_2H$, crystallises in colourless needles, melts at 54°, and is insoluble in water, but soluble in organic solvents or dilute alkalis. It gives a yellow coloration with ferric chloride and a white, flocculent *precipitate* with silver nitrate. The acid does not form an additive compound with bromine.

On distillation with zinc dust, *cyclo*gallipharic acid yields *m*-xylene and naphthalene.

*cyclo*Gallipharic acid is not reduced by sodium or sodium amalgam, but when heated with hydriodic acid and red phosphorus at 100°, yields a *substance* which is half melted at 15°, decolorises bromine water, and gives a white precipitate with ferric chloride. It is considered to be the hydrocarbon corresponding with *cyclo*gallipharic acid.

G. Y.

Aromatic Butadienedicarboxylic Acids. I. HANS STOBBE (*Ber.*, 1904, 37, 2232—2236).—In acid solution, aldehydes react with succinic acid or its esters, yielding paraconic acids, which may be transformed into mono-substituted itaconic acids. In the presence of sodium ethoxide, aldehydes react with esters of succinic acid, yielding $\alpha\delta$-disubstituted butadienedicarboxylic acids or γ-monosubstituted itaconic acids.

Condensations between ketones and esters of succinic acids do not occur in acid solution; in the presence of sodium ethoxide, the condensation is usually between equal number of molecules of the reacting substances, but in a very few cases two molecules of aldehyde react with one of the ester.

Aldehydes also readily condense with the esters of mono- and disubstituted itaconic acids, yielding di- and tri-substituted butadienecarboxylic acids. As a rule, ketones do not react so readily, and the products are tri- and tetra-substituted butadienedicarboxylic acids.

The butadienedicarboxylic acids are sparingly soluble in water and the usual solvents. They are only faintly acid, and can be extracted from solutions of their salts by suitable solvents. Some are colourless, others yellow, and their melting points, as a rule, are above 200°; at this temperature, the majority yield anhydrides. Permanganate oxidises them to oxalic acid and aldehydes or ketones, sodium amalgam reduces them to butanedicarboxylic acids, but towards alkalis they are relatively stable.

J. J. S.

Butadiene Derivatives. II. Coloured Anhydrides of Butadiene-$\beta\gamma$-dicarboxylic Acids. Hans Stobbe (*Ber.*, 1904, **37**, 2236—2240).—Butadiene-$\beta\gamma$-dicarboxylic acids (compare preceding abstract) are readily transformed into anhydrides under the influence of acetyl chloride. These anhydrides are all coloured and often exhibit pleochroism; they are stable in the presence of water or sodium carbonate, but alkali hydroxides gradually hydrolyse them to the alkali salts of the acids. Dark-coloured intermediate products appear to be formed during the hydrolysis. The anhydrides dissolve in piperidine, yielding salts which are soluble in water and from which the free acids can readily be obtained. Under the action of light and heat, the anhydrides undergo changes in colour. This change is only temporary when the exposure is for a short time, but, on prolonged exposure, isomeric anhydrides are obtained.

The temporary change is a case of phototropy (compare Marckwald, Abstr., 1900, ii, 2; Biltz, *ibid.*, ii, 125). The permanent change is most readily brought about in solution and yields isomerides, the constitutions of which have not been determined. J. J. S.

Butadiene Derivatives. III. Dibenzylidenesuccinic Acid. Hans Stobbe and Phokion Naoúm [and, in part, with Karl Kautzsch] (*Ber.*, 1904, **37**, 2240—2249. Compare preceding abstracts).—Dibenzylidenesuccinic acid ($\alpha\delta$-diphenylbutadiene-$\beta\gamma$-dicarboxylic acid) (compare Abstr., 1894, i, 595) may be obtained by the action of an ethereal solution of benzaldehyde on ethyl succinate in the presence of sodium ethoxide free from alcohol or from benzaldehyde and ethyl γ-phenylitaconate in an alcoholic solution of sodium ethoxide. Among the by-products obtained are benzyl alcohol, benzoic acid, phenylitaconic acid, phenylaticonic acid, and an unsaturated *acid*, $C_{17}H_{16}O_3$, melting at 170—171°, and its *ethyl* ester, which melts at 48—50°.

Dibenzylidenesuccinic acid crystallises from ether in glistening, four-sided plates containing a molecule of ether of crystallisation. The *sodium* salt contains $1H_2O$, which it loses at 140—160°. The *silver* salt is anhydrous, and the *barium* salt has the formula

$$4C_{18}H_{12}O_4Ba,7H_2O.$$

The *piperidine* salt melts and decomposes at 181—182° and is readily soluble in water. The *ethyl* ester crystallises in colourless prisms melting at 110·5°.

The *anhydride* obtained by the action of acetyl chloride on the acid forms large, yellow, triclinic crystals melting at 203—204°. It dissolves readily in chloroform and hot benzene and is not hydrolysed by hot water or sodium carbonate solution.

On oxidation, the acid yields oxalic and benzoic acids; acetic and malonic acids do not appear to be formed. Hot alkalis are practically without action on dibenzylidenesuccinic acid.

Both the acid and its ester, when exposed to sunlight in benzene solution and in presence of iodine, are transformed into isomerides.

J. J. S.

Condensation of Acetophenone with Ethyl Malonate. Johan F. Eijkman (*Chem. Centr.*, 1904, i, 1258—1259; from *Chem. Weekblad.*, 1, 349—372).—By the action of ethyl malonate on aceto-

phenone in ethereal solution and in presence of sodium ethoxide, dypnone (compare Delacre and Gesché, Abstr., 1900, i, 603, 604), *a-iso*-dypnopinacolin, phenylmethylcarbinol (compare Stobbes, Abstr., 1901, i, 549), and β-ethylphenacylmalonic acid are formed. Dypnone and *a-iso*dypnopinacolin are also formed by the action of sodium ethoxide on acetophenone. *a-iso*Dypnopinacolin separates from acetone in colourless crystals which melt at 134·5°; it is sparingly soluble in cold ether or alcohol, but more so in the hot solvents. A saturated solution in 99·5 per cent. alcohol contains 0·425 per cent. By the action of bromine in glacial acetic acid or of phosphorus pentachloride it is converted into *a*-dehydro*iso*dypnopinacolin, $C_{32}H_{24}O$, which crystallises from alcohol in colourless needles melting at 174·5° (compare Delacre, *Bull. Acad. roy. Belg.*, 1895, 855). *β-Ethylphenacylmalonic acid*, $COPh{\cdot}CHEt{\cdot}CH(CO_2H)_2$, crystallises from dilute alcohol in colourless crystals and melts and decomposes about 140°; it is sparingly soluble in cold, but more soluble in boiling water or ether, and readily so in alcohol. The *ethyl ester* is a colourless liquid which has a sp. gr. 1·1012 at 22·1° and n_a 1·49555 at 22·1°. By the action of phenylhydrazine on a solution of the free acid in glacial acetic acid, a dibasic *hydrazonic acid*, $C_{19}H_{20}O_4N_2$, is formed, which crystallises from alcohol and melts and decomposes at 162°. If ether is used as a solvent instead of glacial acetic acid, the carboxyl groups are also attacked by the hydrazine and a *diphenylhydrazine* salt of the hydrazonic acid, $C_{31}H_{36}O_4N_6$, is formed. The latter compound is precipitated from its solution in alcohol by light petroleum in the form of a colourless, crystalline powder which melts with liberation of gas at 80°. *β-Ethylphenacylacetic acid*, $COPh{\cdot}CHEt{\cdot}CH_2{\cdot}CO_2H$, crystallises from alcohol in colourless needles, melts at 78·5°, is soluble in ether or benzene, and has a sp. gr. 1·0878 at 79·05° and n_a 1·50742 at 79·05°. The *ethyl ester*, $C_{14}H_{18}O_3$, is a colourless liquid which boils at 175° under 20 mm. pressure, and has a sp. gr. 1·0612 at 17·9° and n_a 1·50548 at 17·9°. The *phenylhydrazone*, $C_{18}H_{20}O_2N_2$, separates from alcohol in colourless crystals and melts at 136°. When β-ethylphenacylacetic acid is warmed with excess of acetyl chloride, it appears to be converted into the enolic form, $OH{\cdot}CPh{:}CEt{\cdot}CH_2{\cdot}CO_2H$, an amorphous acetate, $C_{14}H_{16}O_4$, being obtained, which has a sp. gr. 1·0843 at 78·9° and n_a 1·51107 at 78·9°; it changes slowly into the original acid. *Dibromo-β-ethylphenacylacetic acid*, $C_{12}H_{12}O_3Br_2$, formed by the action of bromine on β-ethylphenacylacetic acid, crystallises from benzene and melts at 150°; the whole of the bromine may be removed by the action of dilute alkalis. By the action of sodium amalgam, β-ethylphenacylacetic acid is reduced to *β-ethylphenylbutyrolactone* $CHEt{<}{\begin{matrix}CHPh-\\CH_2{\cdot}CO\end{matrix}}{>}O$, which crystallises from alcohol in colourless needles melting at 88°; it boils at 165° under 3 mm. pressure, has a sp. gr. 1·0525 at 86·1° and n_a 1·50715 at 86·1°, and is very sparingly soluble in light petroleum. *γ-Phenyl-β-ethylbutyric acid*,

$$CH_2Ph{\cdot}CHEt{\cdot}CH_2{\cdot}CO_2H,$$

prepared by heating the lactone with hydriodic acid of sp. gr. 1·7 at 170—180°, crystallises from alcohol, melts at 22°, boils at 134° under 1 mm. pressure, and has a sp. gr. 1·0339 at 13·4° and n_a 1·50862

at 13·4°; the *calcium* salt, $Ca(C_{12}H_{15}O_2),3H_2O$, is sparingly soluble in water and melts at the temperature of the water-bath. By the dry distillation of β-ethylphenacylacetic acid or β-ethylphenacylmalonic acid with lime, acetophenone is formed, and both these acids on oxidation with potassium permanganate give a nearly quantitative yield of benzoic acid. α-Ethylphenacylmalonic acid, $COPh\cdot CH_2\cdot CEt(CO_2H)_2$ (compare Dittrich and Paal, Abstr., 1889, i, 257), crystallises from chloroform forming a compound of the composition $2C_{13}H_{14}O_5,CHCl_3$. Diphenacylmalonic acid, $C(CH_2\cdot COPh)_2(CO_2H)_2$ (compare Kuess and Paal, Abstr., 1887, 261), also forms a crystalline compound with 1 mol. of chloroform. By the action of phenylhydrazine (1 mol.) on α-ethylphenacylmalonic acid, 2 mols. of water are eliminated and an *acid* is formed which melts at 134° and probably has the composition $N{<}{\substack{NPh-CO\\CPh\cdot CH_2}}{>}CEt\cdot CO_2H$.

When an ethereal solution of the acid is used, however, *diphenylhydrazine α-ethylphenacylmalonate*, $C_{25}H_{30}O_5N_4$, is obtained in the form of a white, crystalline precipitate which melts and liberates gas at 113°. When α-ethylphenacylacetic acid, which is prepared by heating the corresponding malonic acid above its melting point, is reduced by sodium amalgam, α-ethylphenylbutyrolactone,

$$CHPh{<}{\substack{CH_2-\\O\cdot CO}}{>}CHEt,$$

is formed; it crystallises from ether, melts at 30°, and has a sp. gr. 1·0920 at 13·5° and n_α 1·52435 at 13·5°.

Phenylbutyrolactone and ethyl benzoylpropionate have been prepared from benzoylpropionic acid by the usual methods; the former melts at 37° and boils at 128° under 2 mm. pressure, whilst the latter boils at 128° under 2 mm. and at 184° under 22 mm. pressure. The following data have also been experimentally determined, the sp. gr. and n_α being measured in each case at the same temperature:

	Sp. gr.	n_α.	Temp.
Phenylbutyrolactone	1·1554	1·54184	15·4°
	1·1042	1·51591	80·15
Ethyl benzoylpropionate ...	1·1068	1·51408	13·5
Acetophenone..................	1·0297	1·53017	17·6
	0·9781	1·50160	77·6
Phenyl ethyl ketone	1·0133	1·52461	15·7
Phenyl undecyl ketone	0·87935	1·47001	78·5
Phenyl pentadecyl ketone...	0·8692	1·46746	75·9

The values of the molecular refraction and molecular dispersion calculated from the so-called atomic constants do not agree with the results of actual measurement. E. W. W.

Nitrobenzylated Ethyl Acetonedicarboxylates. Fritz Fichter and Chaskel Wortsmann (*Ber.*, 1904, 37, 1992—1997).—On adding an alcoholic solution of ethyl sodioacetonedicarboxylate to a hot alcoholic solution of *p*-nitrobenzyl chloride (1 mol.), *ethyl* as-*di*-p-*nitrobenzylacetonedicarboxylate*, $CO_2Et\cdot C(CH_2\cdot C_6H_4\cdot NO_2)_2\cdot CO\cdot CH_2\cdot CO_2Et$, is obtained; it separates from glacial acetic acid in large, lustrous

crystals, melts at 118—119°, and is hydrolysed by boiling hydrochloric acid to as-*di*-p-*nitrobenzylacetone*, $CH(CH_2\cdot C_6H_4\cdot NO_2)_2\cdot CO\cdot CH_3$, which crystallises from alcohol in thin, flexible, silky needles melting at 108·5—109·5°. Simultaneously with the asymmetrical dicarboxylate is produced s-*di*-p-*nitrobenzylacetone*, $CO(CH_2\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, which crystallises from alcohol or glacial acetic acid in slender, lustrous needles, melts at 136—138°, and is probably formed owing to the hydrolysis by sodium ethoxide of the *dicarboxylate*,

$$CO[CH(CO_2R)\cdot CH_2\cdot C_6H_4\cdot NO_2]_2;$$

the latter substance, however, could not be isolated. The presence of *ethyl* p-*nitrobenzylacetonedicarboxylate*,

$$CO_2Et\cdot CH(CH_2\cdot C_6H_4\cdot NO_2)\cdot CO\cdot CO_2Et,$$

in the oily mother liquors is proved by their giving p-*nitrobenzylacetone*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2Ac$, on hydrolysis with hydrochloric acid; this ketone is isolated by means of its sodium hydrogen sulphite derivative and melts at 40—41°. The acid products of this hydrolysis are *p*-nitrohydrocinnamic acid, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H$, and di-*p*-nitrobenzoylacetic acid.

By acting with 2 mols. of *p*-nitrobenzyl chloride on ethyl sodioacetonedicarboxylate, the same products are obtained as with 1 mol., but using the proportion required for a tri-*p*-nitrobenzyl derivative, *ethyl tri*-p-*nitrobenzylacetonedicarboxylate*,

$$CO_2Et\cdot C(CH_2\cdot C_6H_4\cdot NO_2)_2\cdot CO\cdot CH(CH_2\cdot C_6H_4\cdot NO_2)\cdot CO_2Et,$$

is obtained. It crystallises from glacial acetic acid in lustrous, slightly yellow needles, melts at 167·5—168·5°, and is hydrolysed by hydrochloric acid to form *p*-nitrohydrocinnamic acid and di-*p*-nitrobenzylacetic acid. Together with the tri-*p*-nitrobenzyl derivative there is formed *tetra*-p-*nitrobenzylacetone*,

$$CO[CH(CH_2\cdot C_6H_4\cdot NO_2)_2]_2,$$

which separates from nitrobenzene on adding alcohol in colourless crystals and melts at 194—195°; it is produced by the hydrolysis of a corresponding dicarboxylate. Some *ethyl di*-p-*nitrobenzylacetate*, $CO_2Et\cdot CH(CH_2\cdot C_6H_4\cdot NO_2)_2$, crystallising from alcohol or glacial acetic acid in white needles and melting at 104·5°, was also isolated and was identified by hydrolysing it to the corresponding acid.

W. A. D.

Synthesis of Benzene Derivatives from Ethyl Glutaconate. HANS VON PECHMANN, WILHELM BAUER, and JULIUS OBERMILLER (*Ber.*, 1904, 37, 2113—2122).—*Ethyl* 5-*hydroxy*-2 : 4-*dicarboxydihydro*cyclo*hexadieneacetate*, $OH\cdot C_6H_4(CO_2Et)_2\cdot CH_2\cdot CO_2Et$, produced on condensing ethyl glutaconate with sodium ethoxide, crystallises in colourless needles melting at 82° and gives a deep blue coloration with ferric chloride. The *diethyl ester*, formed by cautiously hydrolysing the triethyl ester with alcoholic potash, crystallises in colourless needles, melts without decomposition at 112—113°, gives a blue coloration with iron chloride, and is very soluble in alkali hydroxides. The *monoethyl ester*, produced from either of these esters by heating with 10 per cent. potassium hydroxide, crystallises in platelets melting and decomposing at 154°.

Ethyl 5-*hydroxy*-2 : 4-*dicarboxyphenylacetate*, obtained by oxidising

the foregoing triethyl ester with bromine, crystallises in colourless needles melting at 81°, gives a cherry-red coloration with ferric chloride, and does not decolorise permanganate; the *acetyl* derivative melts at 59° and does not give a coloration with ferric chloride. The *methyl* ether forms colourless, silky needles melting at 87°.

5-*Hydroxy*-2 : 4-*dicarboxyphenylacetic acid*, prepared by boiling the triethyl ester with potassium hydroxide, crystallises in colourless needles melting at 250—255°; the *acid potassium* salt melts at 212°. When heated with hydrogen chloride at 200°, it forms *m*-hydroxyphenylacetic acid. *Tribromo*-m-*hydroxyphenylacetic acid* is formed either by directly brominating the acid or on saturating the aqueous solution of the dicarboxylic acid with hydrogen bromide; it crystallises in long, colourless needles melting at 237°.

By the condensation of ethyl glutaconate and sodium ethoxide, 4-hydroxyethyl *iso*phthalate is also formed; this melts at 57° and on hydrolysis gives the 4-hydroxy*iso*phthalic acid described by Lawrence and Perkin (*Proc.*, 1901, 17, 47). E. F. A.

Erythrin (Erythric Acid). PAUL JUILLARD (*Bull. Soc. chim.*, 1904, [iii], 31, 610—615).—Erythrin, obtained by the extraction of orchil lichens with neutral solvents, has the formula $C_{40}H_{44}O_{20},2H_2O$, is crystalline, melts at 146—148°, and is slightly soluble in the ordinary solvents. When treated with lime, it absorbs a molecule of water forming *anhydroerythric acid*, $C_{40}H_{46}O_{21}$, which, when dissolved in alcohol, decomposes into "simple erythrin," $C_{20}H_{22}O_{10},H_2O$, which melts at 138° and is the principal constituent of the "erythric acid" obtained by Stenhouse, Hesse, and others by the extraction of lichens with alkaline liquids. These three substances, when dissolved in hot alcohol, furnish picroerythrin and ethyl orsellate. The author proposes to represent these substances as derivatives of orthocarbonic acid, $C(OH)_4$. He assigns to orsellic acid the formula

$$OH\cdot C_6H_3Me\cdot O\cdot C(OH)_3 \ (Me:OH:O\cdot C(OH)_3 = 1:5:3),$$

and represents the combination of erythritol with this to form picroerythrin by the formula

$$OH\cdot C_6H_3Me\cdot O\cdot C(OH){<}^{O}_{O}{>}C_4H_6(OH)_2,$$

whilst to anhydroerythric acid, erythric acid, and the related substances β-picroerythrin, β-orsellic and lecanoric acids, formulæ derived from these are assigned. T. A. H.

***p*-Substituted *o*-Nitrobenzaldehydes.** FRANZ SACHS and EMIL SICHEL (*Ber.*, 1904, 37, 1861—1874. Compare Abstr., 1902, i, 377, 682; this vol., i, 62).—4-*Nitro*-2-*aminobenzaldehyde*,

$$NO_2\cdot C_6H_3(NH_2)\cdot CHO,$$

prepared by reducing 2 : 4-dinitrobenzaldehyde by titanium trichloride (Knecht, Abstr., 1903, ii, 217), crystallises from water in slender needles and melts at 124°. Its *phenylbenzylhydrazone* separates from aqueous alcohol in glistening, violet plates and melts at 155°. Its *semicarbazone* forms reddish-yellow crystals, decomposes at about 390°. Its *oxime* separates from a mixture of acetone and water in bright

yellow crystals and melts at 193°. Its *anil* separates from dilute alcohol in red crystals and melts at 147°.

4-*Chloro-2-nitrobenzaldoxime*, $NO_2\cdot C_6H_3Cl\cdot CH{:}NOH$, prepared from 4-chloro-2-nitrobenzaldehyde, separates from ethyl alcohol in glistening threads and melts at 172°. 1-*Phenyl*-4-p-*chloro*-o-*nitrobenzylidene*-3-*methylpyrazolone*, $NO_2\cdot C_6H_3Cl\cdot CH{:}C<\begin{matrix}CO-NPh\\ CMe{:}N\end{matrix}$, forms dark red crystals and melts at 180°.

4-*Chloro-2-nitrobenzylideneaniline*, $NO_2\cdot C_6H_3Cl\cdot CH{:}NPh$, separates from ethyl alcohol in yellowish-white needles and melts at 93°. β-*Hydroxy*-β-4-*chloro*-2-*nitrophenylethylmethyl ketone*,

$$NO_2\cdot C_6H_3Cl\cdot CH(OH)\cdot CH_2\cdot COMe,$$

prepared by condensation of 4-chloro-2-nitrobenzaldehyde with acetone in presence of trisodium phosphate, crystallises from water in fan-shaped rods and melts at 76°. When its solution is warmed and a few drops of sodium hydroxide or sodium carbonate solution added (compare this vol., i, 325), dichloroindigotin is precipitated as a reddish-violet, flocculent precipitate. 4-*Chloro-2-nitrostyryl methyl ketone*, $NO_2\cdot C_6H_3Cl\cdot CH{:}CH\cdot COMe$, prepared by warming β-hydroxy-β-4-chloro-2-nitrophenylethyl methyl ketone with acetic anhydride and sodium acetate, crystallises from dilute alcohol in stellate rods and melts at 102°.

4-Bromo-2-nitrobenzaldehyde, prepared by heating 2-nitro-4-aminobenzaldoxime with ferric sulphate and hydrobromic acid, is identical with the compound previously prepared by Sachs and Kempf by the application of the Sandmeyer reaction to 2-nitro-4-aminobenzaldoxime. Its *semicarbazone* separates from glacial acetic acid in yellowish-white crystals and melts at 276°. Its *oxime* crystallises from aqueous ethyl alcohol in white scales and melts at 164°. β-*Hydroxy*-β-4-*bromo*-2-*nitrophenylethyl methyl ketone*, $NO_2\cdot C_6H_3Br\cdot CH(OH)\cdot CH_2\cdot COMe$, melts at 92° and yields dibromoindigotin by the action of sodium hydroxide or sodium carbonate. 4-*Bromo-2-nitrostyryl methyl ketone* crystallises from dilute alcohol in snow-white needles and melts at 109°. 4-*Bromo-2-nitrobenzylideneaniline* separates from dilute alcohol in silky needles and melts at 105°.

2 : 4-*Dinitrobenzaldehyde acetal*, $C_6H_3(NO_2)_2\cdot CH(OMe)_2$, prepared by the action of a solution of hydrogen chloride in methyl alcohol on 2 : 4-dinitrobenzaldehyde, boils at 183—185° under 13 mm. pressure. 1-*Phenyl*-4-*dinitrobenzylidene*-3-*methylpyrazolone*,

$$C_6H_3(NO_2)_2\cdot CH{:}C<\begin{matrix}CO-NPh\\ CMe{:}N\end{matrix},$$

melts at 160°.

1-*Phenyl*-4-o-*nitrobenzylidene*-3-*methylpyrazolone* melts at 154°.

When a solution of *p*-chloro-*o*-nitrobenzylideneaniline in toluene is exposed to direct sunlight for four weeks, snow-white crystals of 4-*chloro-2-nitrosobenzanilide*, $NO\cdot C_6H_3Cl\cdot CO\cdot NHPh$, melting at 170°, separate. *Bis*-o-*nitrobenzylidene*-p-*phenylenediamine*,

$$C_6H_4(N{:}CH\cdot C_6H_4\cdot NO_2)_2,$$

prepared from *o*-nitrobenzaldehyde, *p*-phenylenediamine hydrochloride, and sodium acetate, separates from acetone in needles and melts at

208°. When first prepared, it is bright yellow; it gradually becomes, in the course of a dull winter's day, golden-bronze and then greyish-green, and after two days greyish-black.

Bisdinitrobenzylidene-p-*phenylenediamine*,

$$C_6H_4[N\colon CH\cdot C_6H_3(NO_2)_2]_2,$$

separates from toluene in golden-yellow needles and melts at 252°. *Bis*-p-*chloro*-o-*nitrobenzylidene*-p-*phenylenediamine*,

$$C_6H_4(N\colon CH\cdot C_6H_3Cl\cdot NO_2)_2,$$

melts at 230°. It is at first bright yellow; this colour gradually changes through golden-bronze and green to brownish-black under the influence of light.

4-*Bromo*-2-*nitrosobenzoic acid*, prepared by exposing a solution of *p*-bromo-*o*-nitrobenzaldehyde in a mixture of benzene and toluene to the action of light of $2\frac{1}{2}$ weeks, separates in snow-white, rhombic plates, which melt at 222—225°. *Ethyl 4-bromo-2-nitrosobenzoate*, $NO\cdot C_6H_3Br\cdot CO_2Et$, prepared by the action of light on an alcoholic solution of *o*-nitro-*p*-bromobenzaldehyde, separates from alcohol in rhombic prisms and melts at 155°. It condenses with *p*-nitrobenzylcyanide to form the 2-*carbethoxy*-5-*bromoanil* of p-*nitrobenzoylcyanide*, $NO_2\cdot C_6H_4(CN)\cdot C\colon N\cdot C_6H_3Br\cdot CO_2Et$, which melts at 144°.

4-*Chloro*-2-*aminobenzaldehyde*, prepared by reducing 4-chloro-2-nitrobenzaldehyde with titanium chloride, crystallises from alcohol in long needles and melts at 86°. Its *phenylhydrazone* separates from dilute ethyl alcohol in white leaflets, with a mother-of-pearl lustre, and melts at 230°. 1-*Phenyl*-4-p-*chloro*-o-*aminobenzylidene*-3-*methylpyrazolone* derivative melts at 265°. A. McK.

Preparation of Four Isomeric Methylionones. Haarmann and Reimer (D.R.-P. 150827).—In the preparation of alkylated ψ-ionones, the aldehyde group of the citral may react either with the methyl group of the ketone, or with the adjoining methylene group, and each of the isomerides thus produced may occur in two forms, corresponding with α- and β-ionones. Both α- and β-methylionones (Abstr., 1902, i, 471) contain two isomerides, one of which (the *a*-form) dissolves readily in sodium hydrogen sulphite, the *b*-form being sparingly soluble. ψ-Methylionone may in a similar manner be separated into a readily and a more sparingly soluble constituent, which may then be converted into the corresponding methylionones.

a-α-*Methylionone* boils at 137—142° (uncorr.) under 15 mm. pressure and has a sp. gr. 0·927 and n_D 1·5009 at 20°; its *semicarbazone* melts at 144°. b-α-*Methylionone* boils at 135—140° under 15 mm. pressure, and has a sp. gr. 0·931 and n_D 1·5003 at 20°; the *semicarbazone* melts at 202°.

a-β-*Methylionone* boils at 145—151° under 15 mm. pressure, and has a sp. gr. 0·935 and n_D 1·5097 at 20°; its *semicarbazone* melts at 138—139°. b-β-*Methylionone* boils at 135—140° under 15 mm. pressure, and has a sp. gr. 0.936 and n_D 1·5073 at 20°; the *semicarbazone* melts at 175—176°. C. H. D.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. Elmer P. Kohler (*Amer. Chem. J.*, 1904, 31, 642—661).—A further study of the substance obtained by the

interaction of benzylideneacetophenone and magnesium phenyl bromide (Abstr., 1903, i, 483) has shown that this product is not diphenylstyrylcarbinol, but consists of the isomeric ketone, *diphenylpropiophenone*, $CHPh_2 \cdot CH_2 \cdot COPh$, which can also be prepared by the condensation of benzylideneacetophenone with benzene in presence of concentrated sulphuric acid. Its *phenylhydrazone* crystallises in pale yellow needles and melts at 137°; the *oxime* melts at 131°, and by the action of phosphorus pentachloride is converted into *diphenylpropionanilide*, which melts at 167°. When diphenylpropiophenone is treated with magnesium phenyl bromide, *diphenylethyldiphenylcarbinol*,

$$CHPh_2 \cdot CH_2 \cdot CPh_2 \cdot OH,$$

is produced, which crystallises in needles, melts at 95—96°, and is readily soluble in alcohol or ether; the same substance is formed by the action of magnesium phenyl bromide on methyl diphenylpropionate. *Bromodiphenylpropiophenone*, $CHPh_2 \cdot CHBr \cdot COPh$, prepared by the action of bromine on the magnesium compound formed in the reaction between benzylideneacetophenone and magnesium phenyl bromide, crystallises in colourless needles and melts at 173°. *Benzoyltriphenylpropenol*, $CHPh_2 \cdot CH{:}CPh \cdot OBz$, obtained by the action of benzoyl chloride on the magnesium compound, crystallises in long, transparent needles, melts at 220°, and is soluble in hot chloroform or hot benzene; when warmed with a strong solution of potassium hydroxide containing a little alcohol, it is decomposed with formation of diphenylpropiophenone and potassium benzoate.

When benzylideneacetophenone is treated with magnesium methyl iodide, phenylbutyrophenone is produced, which melts at 74° and yields an *oxime* melting at 93°.

*Diphenyl*iso*butyrophenone*, $CHPh_2 \cdot CHMe \cdot COPh$, obtained by the interaction of benzylidenepropiophenone and magnesium phenyl bromide, crystallises in needles or plates, melts at 105°, and is readily soluble in alcohol or ether and moderately so in light petroleum; the *oxime* melts at 145°.

ββ-Diphenylbutyrophenone, $CPh_2Me \cdot CH_2 \cdot COPh$, prepared by the action of magnesium phenyl bromide on dypnone, crystallises in thick prisms, melts at 103°, and dissolves readily in alcohol, acetone, or ether; the *oxime* melts at 163°.

When the product of the interaction of magnesium phenyl bromide and benzylideneacetone is decomposed with ice and hydrochloric acid, the tertiary *alcohol*, $CHPh{:}CH \cdot CPhMe \cdot OH$, is produced as an oil which, on oxidation with cold neutral solution of potassium permanganate, yields benzoic and α-phenyl-lactic acids.

By the action of magnesium phenyl bromide on cinnamaldehyde, an oily product, probably the secondary *alcohol*, $CHPh{:}CH \cdot CHPh \cdot OH$, is obtained, which, on oxidation, is converted into benzylideneacetophenone. Magnesium phenyl bromide reacts in a similar manner with α-bromocinnamaldehyde. E. G.

Action of Nitrous Gases on 1 : 3-Diketones. HEINRICH WIELAND and SIEGFRIED BLOCH (*Ber.*, 1904, 37, 1524—1536).—*Bisnitrosodibenzoylmethane*, $CHBz_2 \cdot N_2O_2 \cdot CHBz_2$, obtained on passing the nitrous fumes evolved from arsenious oxide and nitric acid into an

absolute ethereal solution of dibenzoylmethane, forms a white powder which is insoluble in most solvents and melts and decomposes at 125°; it is decomposed by boiling alcohol or more easily by cold alcoholic potassium hydroxide or ammonia, giving the oxime $CBz_2{:}N{\cdot}OH$ (von Pechmann, Abstr., 1891, 318). This oxime is rapidly hydrolysed by 20 per cent. sodium hydroxide forming benzoic acid and hydrogen cyanide. From the ethereal mother liquors of bisnitrosodibenzoylmethane, diphenyl triketone, $COPh{\cdot}CO{\cdot}COPh$ (von Pechmann, *loc. cit.*), separates as the crystalline hydrate. In order to convert the whole of the dibenzoylmethane into the triketone, the bisnitroso-derivative is converted by cold dilute alcoholic potassium hydroxide into the foregoing oxime, and this is then decomposed in ethereal solution by the nitrous gases.

When *p*-nitrodibenzoylmethane is exposed in benzene solution to the action of the nitrous fumes, it does not give a bisnitroso-derivative, but is converted directly into p-*nitrodiphenyl triketone*,

$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CO{\cdot}COPh,$$

which crystallises from benzene or carbon disulphide and melts at 98—99°; it readily absorbs water in alcoholic glacial acetic acid solution to form the *hydrate*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}C(OH)_2{\cdot}COPh$, which melts indefinitely at about 100°. By boiling water, the triketone is hydrolysed to *p*-nitrobenzoic acid, and with phenylhydrazine, it gives the *diphenylhydrazone*, $NO_2{\cdot}C_6H_4{\cdot}C(N_2HPh){\cdot}CO{\cdot}C(N_2HPh){\cdot}C_6H_5$, which crystallises from glacial acetic acid in vermilion-coloured needles and melts at 219°.

Bisnitrosobenzoyl-p-*anisoylmethane*, $(OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHBz)_2N_2O_2$, prepared from anisoylbenzoylmethane in absolute ethereal solution, melts and decomposes at 115—116°; from the mother liquors of this substance, *phenylanisyltriketone*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CO{\cdot}COPh$, is obtained, crystallising from benzene and melting at 65°; the *oxime*,

$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}C(N{\cdot}OH){\cdot}COPh,$$

forms colourless leaflets and melt at 127°.

Bisnitrosobenzoylacetone, $N_2O_2(CHAcBz)_2$, prepared from benzoylacetone, melts and decomposes at 65°; by alcohol at 30°, it is transformed into the oxime, $COPh{\cdot}CAc{:}N{\cdot}OH$, but the product is only purified with difficulty. W. A. D.

Quinonesulphonic Acid. GUSTAV SCHULTZ and R. STÄBLE (*J. pr. Chem.*, 1904, [ii], 69, 334—346).—4-*Aminophenol*-3-*sulphonic acid* is obtained by acting on *m*-phenolsulphonic acid with diazobenzene chloride in presence of sodium hydroxide and reducing the resulting *azo*-compound with stannous chloride and hydrochloric acid. It crystallises in sheaves of delicate, glistening needles, commences to blacken at 270°, decomposes at 285°, and is more soluble in water than 4-aminophenol-2-sulphonic acid or 2-aminophenol-4-sulphonic acid. It reduces ammoniacal silver solutions, gives a brownish-violet coloration with neutral ferric chloride, yields quinone on energetic oxidation, and forms bromanil when heated with an excess of bromine. The *potassium* and *barium* salts are described. The action of nitrous acid on 4-aminophenol-3-sulphonic acid leads to the formation of 4 *diazophenol*-3-*sulphonic acid*, $OH{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}SO_3H$, which crys-

tallises in small, colourless tetrahedra or prisms, loses H_2O at 110°, and melts and decomposes at 189°. It is only slightly soluble in water, gives dyes with β-naphthol and sodium β-naphtholdisulphonate in alkaline solution, is reduced to aminohydroxybenzenesulphonic acid by stannous chloride and hydrochloric acid, and when heated at 180° with sulphuric acid yields quinol. Diazophenolsulphonic acid is also formed by the action of nitrous acid on 4-aminophenol-3-sulphonic acid (compare Bennewitz, *J. pr. Chem.*, 1873, [ii], 8, 52).

Quinonesulphonic acid is formed on oxidation of quinolsulphonic acid (Seyda, Abstr., 1883, 1115) by lead peroxide and sulphuric acid. A small amount of the free acid (?) is obtained in yellow, transparent prisms on addition of alcohol and ether. On addition of potassium chloride to the oxidation product, the *potassium* salt, $C_6H_3O_2\cdot SO_3K$, is precipitated. Quinonesulphonic acid is also formed to a small extent by oxidation of 4-aminophenol-3-sulphonic acid, but a good yield is obtained by oxidation of the isomeride [$OH : SO_3H : NH_2 = 1 : 2 : 4$] with sulphuric acid and lead peroxide, when part of the product separates as the *ammonium* salt, $C_6H_3O_2\cdot SO_3NH_4$, and the remainder is precipitated by addition of potassium chloride. The potassium salt crystallises in scarlet prisms and decomposes at 235°; the ammonium salt forms golden, microscopic plates and decomposes at 190—195°. These salts give a greenish-black coloration with ferric chloride in aqueous solution, reduce ammoniacal silver solutions, and form quinhydrone with quinol in aqueous solution. The potassium salt is reduced by sulphur dioxide, with formation of potassium quinolsulphonate. With amines, the potassium and ammonium salts form anilino-compounds: with aniline, a brown, flocculent *precipitate*, soluble in concentrated sulphuric acid to a violet solution; with *p*-toluidine, a brown *precipitate* which dissolves in sulphuric acid to a dark blue solution; with diphenylamine, a bluish-green precipitate, soluble in sulphuric acid with a blue colour; with *m*-phenylenediamine, an intense red coloration in aqueous solution. G. Y.

Uses of Naphthaquinonesulphonic Acid. PAUL EHRLICH and C. A. HERTER (*Zeit. physiol. Chem.*, 1904, 41, 379—392. Compare Witt, Abstr., 1892, 196; Böninger, *ibid.*, 1894, i, 199).—Witt's 1 : 2-naphthaquinone-4-sulphonic acid in the form of its sodium derivative readily reacts with aromatic amines yielding compounds of the type of anilinonaphthaquinone, $C_6H_4<\begin{matrix}CO\text{——}C\cdot OH \\ C(NPh)\cdot CH\end{matrix}$, in the form of red precipitates. The reaction is extremely delicate, and is given by most aromatic amines except when several strongly negative groups are present in the benzene ring. Aminocarboxylic acids, aminosulphonic acids, diamines and amines derived from naphthalene give similar reactions.

The sulphonic acid also yields characteristic colorations in the presence of sodium carbonate with methylene derivatives of the type of ethyl acetoacetate, deoxybenzoin, and cyanoacetamide. Further, resorcinol, phloroglucinol, aliphatic primary amines, secondary amines, peptones, tyrosine, uric acid, &c., give colorations with the acid.

The sulphonic acid is extremely useful for locating aniline or other compounds which have been injected into the animal system. The dyes obtained by condensing the quinone mono- or di-sulphonic acid with dimethyl-*p*-phenylenediaminethiosulphonic acid are extremely useful for staining different tissues. The organs are not coloured when both reacting substances are injected or when the sulphonic acid is injected and the section treated with an amine. This is probably due to the reduction of the quinonesulphonic acid to a quinol derivative in the animal system.

1 : 2-Naphthaquinone-4 : 6-disulphonic acid reacts in much the same manner as the mono-sulphonic acid, and the condensation products are soluble in alkalis. J. J. S.

Preparation of Dyes of the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 151018).—The sulphonic acids of aromatic amines condense with halogenated hydroxyanthraquinones to form dyes. Thus bromopurpurin, prepared by brominating purpurin in boiling acetic acid, chloropurpurin, prepared by chlorinating purpurin suspended in hydrochloric acid, or chloroalizarin may be heated with sodium sulphanilate at 200° under pressure, forming bronze-coloured crystals. C. H. D.

Reduction of Cineole. HERMANN THOMS and B. MOLLE (*Arch. Pharm.*, 1904, 242, 181—194).—Attempts to reduce cineol, $C_{10}H_{18}O$, with various reducing agents only gave a satisfactory result when the substance was heated with hydriodic acid of sp. gr. 1·96 in the presence of a slight excess of metallic mercury, the sealed tubes containing the mixture being heated gradually to 220—225°, maintained for an hour at that temperature, and then allowed to cool gradually. In these circumstances, only 20 per cent. of the tubes burst. The gas formed consisted chiefly of hydrogen, but contained a little carbon dioxide and hydrogen iodide. The liquid product of the reaction was distilled with steam, and the oil which distilled was freed from mercuric iodide by allowing it to remain with a spiral of reduced copper, and then fractionated. Its chief constituent was a hydrocarbon, $C_{10}H_{18}$, named *cinolene*; this boils at 165—167° under 753 mm. pressure and has sp. gr. 0·8240 at 18°, 0·8227 at 20·5°; n_D 1·45993; and is optically inactive. When treated with bromine in chloroform solution, it does not merely form an additive compound, but evolves hydrogen bromide. When it is allowed to remain with hydrogen iodide in acetic acid solution at 0° and the solution then heated with silver acetate, an *acetate*, $C_{10}H_{19}\cdot OAc$, seems to be formed to some extent; and this, when hydrolysed with alcoholic potassium hydroxide, seems to yield an *alcohol*, $C_{10}H_{19}\cdot OH$. Concentrated sulphuric acid converts the hydrocarbon into α : 2-cymenesulphonic acid. It was not found possible to prepare a hydrochloride, nitrosochloride, nitrosite, or nitrosate; neither could a definite product be obtained by oxidation. Probably the hydrocarbon has the constitution $CHMe_2\cdot CH{<}{\substack{CH{=}CH \\ CH_2\cdot CH_2}}{>}CHMe$.

Accompanying this product of the reduction of cineole is another

hydrocarbon $(C_{10}H_{16})_x$, which boils at 200—245° under 22 mm. pressure and resembles vaselin in appearance. C. F. B.

A New Method of preparing Alkyl and Alkylidene Derivatives of Cyclic Ketones. Alkyl Derivatives of Menthone. ALBIN HALLER (*Compt. rend.*, 1904, 1139—1142).—Sodamide reacts with cyclic ketones according to the equation $R<\begin{matrix}CH_2\\|\\CO\end{matrix} + NaNH_2 = R<\begin{matrix}CHNa\\|\\CO\end{matrix} + NH_3$. The product is free from the sodium derivative of the corresponding alcohol and is therefore suitable for preparing pure alkyl derivatives of the ketone. The alkylmenthones may be prepared from menthone in one operation. A dry ethereal solution of the ketone is mixed with finely-powdered sodamide and heated until ammonia ceases to be evolved. A slight excess of an alkyl haloid is then added and the mixture again warmed until the precipitation of sodium haloid is complete. Finally, the ethereal solution is thoroughly washed with water, dried over anhydrous magnesium sulphate, and distilled. The residue is fractionated under reduced pressure. The alkylmenthones are colourless liquids insoluble in water and aqueous alkali hydroxide, but soluble in organic solvents. The following derivatives were prepared from a menthone which gave α_D $-26°18'$ when examined in a layer of 1 decimetre length.

	Boiling point.	α_D for $l=1$ decimetre.
Methylmenthone...	96—97° under 13 mm. pressure	+20°18′
Ethylmenthone ...	101—102 „ 13 „	+38°
Propylmenthone ...	128—132 „ 19 „	+39°20′
*iso*Butylmenthone..	124—128 „ 10 „	+45°
*iso*Amylmenthone..	138—143 „ 10 „	+31°48′
Allylmenthone ...	134—137 „ 20 „	+25°42′

The inversion of rotatory power on passing from menthone to the alkyl derivatives is no doubt due to the action of alkali hydroxide on the original ketone; in fact, it was found that a dextrorotatory menthone, is obtained by acidifying the sodium salt prepared from the lævorotatory variety. When an alkyl group is introduced into menthone a new asymmetric carbon atom is formed in the molecule; it is probable, therefore, that the above derivatives are not homogeneous, but consist of two or more optical isomerides. Sodium menthone reacts with aromatic aldehydes, and derivatives have been prepared from benzaldehyde and anisaldehyde. S. S.

Preparation of Hydroxymethylene Compounds. JULIUS W. BRÜHL (*Ber.*, 1904, 37, 2069—2080).—Hydroxymethylene compounds may be obtained by the action of sodium methoxide free from methyl alcohol and prepared by the method recently described (active sodium methoxide, this vol., i, 545) on *o*-halogenated ketones.

A good yield (90 per cent.) of Claisen's hydroxymethylenecamphor may be obtained by dropping a benzene solution of *o*-dibromocamphor,

melting at 61°, into active sodium methoxide suspended in boiling benzene and kept well agitated. The same compound is obtained when *o*-bromo- or chloro-camphor is used, but the yield is not so good. Neither sodium methoxide containing methyl alcohol of crystallisation nor the commercial product can be employed in place of the so-called "active" form, and the *o*-halogenated derivatives of camphor cannot be replaced by isomerides, for instance, by *β*-dibromocamphor.

o-Bromomenthone under similar treatment yields hydroxymethylene-menthone, $C_8H_{16}<\begin{smallmatrix}C:CH\cdot OH\\ |\\ CO\end{smallmatrix}$.

The reaction is represented as:

$$C_8H_{14}<\begin{smallmatrix}CBr_2\\ |\\ CO\end{smallmatrix} + 3CH_3\cdot ONa = C_8H_{14}<\begin{smallmatrix}C:CH\cdot ONa\\ |\\ CO\end{smallmatrix} + 2NaBr + 2CH_3OH.$$

J. J. S.

The Camphor Group. I and II. JULIUS W. BRÜHL [and MAX RÜDIGER] (*Ber.*, 1904, 37, 2156—2163; 2163—2178. Compare this vol., i, 139, 435, 436, and preceding abstract).—Iodine has no action on hydroxymethylenecamphor in indifferent solvents; in neutral aqueous solution, *a-iodoformylcamphor*, $C_8H_{14}<\begin{smallmatrix}CI\cdot CHO\\ |\\ CO\end{smallmatrix}$, is precipitated, and crystallises from acetic acid on addition of water in glistening, white leaflets, melting at 67—68°. It darkens on exposure to light, especially in solution. Cold concentrated hydrochloric acid dissolves it to a yellow solution, from which it is precipitated unaltered by water. Sodium hypoiodite converts it into *aa-di-iodocamphor*, $C_8H_{14}<\begin{smallmatrix}CI_2\\ |\\ CO\end{smallmatrix}$, which forms yellow leaflets resembling iodoform, but without odour, and melts at 108—109°. It is also obtained from hydroxymethylenecamphor and iodine in alkaline solution. Sodium methoxide decomposes its solution in benzene, forming camphor and a small quantity of hydroxymethylenecamphor.

a-Iodocamphor, $C_8H_{14}<\begin{smallmatrix}CHI\\ |\\ CO\end{smallmatrix}$, prepared by boiling iodoformylcamphor with sodium methoxide in methyl alcohol, crystallises from dilute alcohol in long, colourless needles and melts at 42—43° to a colourless liquid, which only becomes brown at 200°. It is quite stable at the ordinary temperature. Sodium methoxide in xylene forms principally hydroxymethylenecamphor. The same iodocamphor is obtained on boiling di-iodocamphor with potassium hydroxide.

On dissolving magnesium in an ethereal solution of *a*-bromocamphor, and adding iodine in small portions at a time, *a*-iodocamphor is obtained to the extent of 22 per cent., the remainder forming the insoluble camphor magnesium bromide, $C_8H_{14}<\begin{smallmatrix}CH\\ ||\\ C\cdot O\cdot MgBr\end{smallmatrix}$ (compare Malmgren, Abstr., 1903, i, 710, and Brühl, this vol., i, 435). *a*-Chlorocamphor forms an insoluble magnesium compound, but no iodocamphor.

Sodamide reacts slowly with camphor, and the product absorbs

iodine, forming α-iodocamphor, but only to the extent of 15 per cent. An almost quantitative yield of iodocamphor is obtained by the action of sodium powder on an ethereal solution of camphor at the ordinary temperature and addition of iodine to the product. Some borneol and small quantities of condensation products are also obtained.

Bromine reacts with a neutral solution of hydroxymethylenecamphor, forming α-bromoformylcamphor (compare Bishop, Claisen, and Sinclair, Abstr., 1895, i, 62; and Aschan and Brühl, Abstr., 1894, i, 613). In alkaline solution, α-bromocamphor is produced.

Hydroxymethylenementhone reacts with bromine in similar manner to hydroxymethylenecamphor. *α-Bromoformylmenthone*,

$$C_8H_{16}<\begin{matrix}CBr\cdot CHO\\ | \\ CO\end{matrix},$$

forms an unstable, slightly yellow oil, which could be neither distilled nor crystallised. *α-Bromomenthone*, $C_8H_{16}<\begin{matrix}CHBr\\ | \\ CO\end{matrix}$, forms a colourless oil, rapidly becoming dark, and decomposing when heated under reduced pressure, but distilling in a current of steam.

C. H. D.

Metallo-organic Syntheses in the Camphor Group. Giuseppe Oddo (*Ber.*, 1904, **37**, 1569—1572).—The process described by Malmgren (Abstr., 1903, i, 103, 710) for preparing dicamphor and dicamphorquinone from bromocamphor by the use of magnesium does not give a satisfactory yield, but by modifying the conditions a better result may be obtained with magnesium than with the old method in which sodium was used.

W. A. D.

α-Anhydropulegonehydroxylamine. Friedrich W. Semmler (*Ber.*, 1904, **37**, 2282—2289. Compare this vol., i, 437).—The action of benzaldehyde and sodium ethoxide on α-anhydropulegonehydroxylamine leads to the formation of a *benzylidene* derivative,

$$C_{10}H_{15}ON{:}CHPh,$$

which melts at 105—106° and forms a *picrate*, $C_{17}H_{21}ON,C_6H_3O_7N_3$, melting at 125—126°.

The tetrahydro-base forms a *thiocarbamide*, $C_{10}H_{20}ON\cdot CS\cdot NHPh$, which melts at 132°, effervesces when heated above its melting point, and then melts again at about 170°. The tetrahydro-base is also obtained by reducing pulegonehydroxylamine, or Beckmann and Pleissner's keto-amine (see Harries and Röder, Abstr., 1898, i, 573). The keto-amine distils unchanged at 99—100° under 10 mm. pressure.

G. Y.

Action of Paraformaldehyde on Sesquiterpenes. Pierre Genvresse (*Compt. rend.*, 1904, **138**, 1228—1229).—Caryophyllene, clovene, and cadinene form compounds with formaldehyde which have alcoholic functions. The *compound* with caryophyllene, $C_{16}H_{26}O$, obtained by heating 1 mol. of caryophyllene with 1 mol. of trioxymethylene in a Pfungst tube at 180—200° for 10 hours, is a golden-yellow, slightly viscous liquid boiling at 177—178° under 15 mm.

pressure, has no odour, is soluble in alcohol, ether, or acetic acid, has a sp. gr. of 0·997 at 0°, α_D −7°40′ in a 4·93 per cent. chloroform solution at 21°, and n_D 1·508; it combines with one molecular proportion of bromine. The *acetate* boils at 185° under 15 mm. pressure, is soluble in ether, alcohol, or chloroform, has a sp. gr. 0·9969 at 0°, α_D +20°33′ in 11·7 per cent. chloroform solution at 18°, and n_D 1·490; it combines with 1 mol. of bromine.

The *compound* with clovene, $C_{16}H_{26}O$, boils at 170° under 12 mm. pressure, has a sp. gr. 1·001 at 0°, n_D 1·5105, α_D − 7°12′ in 6·03 per cent. chloroform solution at 20°; it combines with 1 mol. of bromine. In each case, the molecular refraction points to one double linking in the molecule.

The *compound* with cadinene, $C_{16}H_{26}O$, boils at 180° under 15 mm. pressure, is an odourless, golden-yellow liquid, has a sp. gr. 0·993 at 0°, n_D 1·521, α_D − 17°54′ in 7·6 per cent. chloroform solution at 20°; it combines with 2 mols. of bromine, and its molecular refraction points to the presence of two double linkings. M. A. W.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Centr.*, 1904, i, 1263—1265; from Schimmel's *Geschäftsber.*, April, 1904. Compare Abstr., 1902, i, 550; 1903, i, 185 and 569).—Apopin oil has been found by K. Keimazu (*J. Pharm. Soc. Japan*, August, 1903) to contain formaldehyde, *d*-pinene, and apopinol. *Apopinol*, $C_{10}H_{18}O$, is not identical with linalool; it boils at about 200°, and, on oxidation with chromic acid, yields citral. The oil is distinguished from camphor oil, which it very much resembles, by the presence of formaldehyde.

Bay oil, prepared from leaves from the Bermudas, differs from the distillate from the West Indian plant mainly in its higher sp. gr., which is 1·0301 at 15°, and its greater solubility in 80 per cent. alcohol. Cananga oil, obtained from fresh dried leaves of trees cultivated in Bangkok, had a sp. gr. 0·9200 at 15°, $[\alpha]_D$ − 51°40′, acid number 1·82, and ester number 34·17; it dissolved in 0·5 volume of 95 per cent. alcohol, but not in 10 volumes of 90 per cent. alcohol.

The determination of cinnamaldehyde in samples of the aldehyde or of Cassia oil by Hanus' method (Abstr., 1903, ii, 768) gives values which agree with those obtained by the sodium hydrogen sulphite method, but in the case of Ceylon cinnamon oil there is a difference which may amount to 8 per cent. between the results obtained by the two methods. Hanus' method is suitable for the determination of the aldehyde in cinnamon bark.

Oil of Cassia flowers, obtained by distilling the pomade prepared from the flowers of *Acacia farnesiana* with steam, removing the fatty acids and salicylic acid and again rectifying with steam, had a sp. gr. 1·0475 at 15°, n_D 1·51331 at 20°, and saponification number 176; it was optically inactive and contained methyl salicylate, *p*-cresol, benzaldehyde, benzyl alcohol, anisaldehyde, and a ketone, which has an odour similar to that of menthone, together probably also with cuminaldehyde. The oil of citronella recently supplied by the firm has been found to be adulterated with Russian petroleum. Since Bamber's method of detection is not quite accurate, the oil is tested for petroleum by treating it with 80 per cent. alcohol, and again after adding 5 per

cent. of petroleum; there should be no separation of oil in either case. Cypress oil, according to Soltmann, contains *d*-pinene, cypress camphor, furfuraldehyde, *d*-camphene, *d*-sylvestrene, *p*-cymene, sabinol (?), a terpene alcohol, which has the odour of roses, *d*-terpineol melting at 35°, and a ketone, which forms a semicarbazone melting at 177—178°. The *d*-terpineol is present in the form of an ester, which is probably the acetate.

A fraction obtained from an oil prepared from *Eucalyptus globulus* contained terpineol and *iso*borneol, but not fenchyl alcohol. *iso*Amyl alcohol was found in the portions of the oil which boil at lower temperatures. A eucalyptus oil prepared from the same plant also yielded a sesquiterpene alcohol, $C_{15}H_{26}O$, which crystallises from 70 per cent. alcohol in colourless needles melting at 88·5°; it boils at 283° under 755 mm. pressure, and has $[\alpha]_D - 35°29'$ in chloroform solution. When heated with dehydrating agents, and especially with a 90 per cent. solution of formic acid, this alcohol yields a mixture of two sesquiterpenes, of which one boils at 247—248° under 748 mm. and at 102—103° under 6 mm. pressure; it has a sp. gr. 0·8956 at 15°, n_D 1·49287 at 20°, and $[\alpha]_D - 55°48'$. The other sesquiterpene boils at 265·5—266° under 755 mm. pressure, and has a sp. gr. 0·9236 at 15°, n_D 1·50602 at 20°, and $[\alpha]_D + 58°40'$.

The oil prepared from needles of the silver fir contains up to about 3 per cent. of lauraldehyde, and probably also decaldehyde. The semicarbazone of the former melts at 101·5—102·5°. The portion of the oil of *Reunion geranium*, which boils below the boiling point of citronella oil, consists mainly of menthone; amyl alcohol, *l*-pinene, linalool, and a small quantity of phellandrene were also detected. An apparently pure sample of ginger grass oil, which had a sp. gr. 0·9380 at 15°, $[\alpha]_D + 22°40'$, saponification number 24, and a saponification number for acetyl 166, did not give the phellandrene reaction directly although it contained phellandrene. The oil consisted mainly of geraniol and an unknown alcohol, $C_{10}H_{16}O$, which has an odour similar to that of linalool. This alcohol boils at 92—93° under 5 mm. pressure, has a sp. gr. 0·9503 at 15°, $[\alpha]_D + 8°40'$, n_D 1·49735 at 20°, and forms an acetate, which has the odour of curled mint and boils at 90—91° under 4 mm. pressure. The acetate has a sp. gr. 0·9725 at 15°, $[\alpha]_D - 4°30'$, and n_D 1·47615 at 20°. The acid obtained by saponifying the oil melts at 106—107° and forms a very sparingly soluble silver salt, which contains 38·9 per cent. of silver.

The fraction of camphor oil boiling at 210—220° contains borneol. Butyric acid has been detected in French oil of lavender, and the neutral products of the saponification of the oil probably contain *iso*amyl alcohol. The oil prepared from *Monodora myristica* consists chiefly of phellandrene; it has a sp. gr. 0·859 at 15°, $[\alpha]_D - 117°40'$, acid number 1·36, and ester number 3·4. In a sample of oil of patchouli, which had a sp. gr. 0·9769 at 15°, $[\alpha]_D - 55°45'$, acid number 2·2, and saponification number 4·2, benzaldehyde, eugenol, and cinnamaldehyde were detected together with an alcohol, a ketone, and two bases which have not yet been identified. The semicarbazone of the ketone melted at 134—135°. No evidence as to the nature of the odoriferous principle of the oil was obtained, and cadinene did not appear to be present.

Patchoulene, prepared from the oil by means of formic acid, boils at 255—256° and has a sp. gr. 0·9334 at 15° and $[\alpha]_D - 36°52'$. Pimento oil contains cineol, *l*-phellandrene, caryophellene, eugenol, eugenol methyl ether, and palmitic acid, together probably also with small quantities of terpene alcohols.

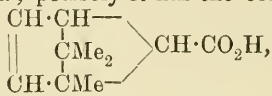
In addition to several South Australian eucalyptus oils and cajeput oils, the following new oils are described. Yomugi oil is more probably an oil from a kind of Artemisia or chrysanthemum; it has a sp. gr. 0·9126 at 15°, $[\alpha]_D - 18°15'$, acid number 1·32, and ester number 16·19. Kuromoji oil is pale yellow and contains cineol, and probably also linalool; it has a sp. gr. 0·8947 at 15°, $[\alpha]_D - 14°29'$, and ester number 29·87. May oil from Porto Rico, prepared from *Calyptranthes paniculata* (*Myrtaceæ*), contained 62·5 per cent. of citral, and had a sp. gr. 0·9509 at 15° and $[\alpha]_D - 1°52'$. A pale yellow oil from *Mentha citrata* (Bergamot mint) from Florida, had a sp. gr. 0·8826 at 15°, $[\alpha]_D - 5°35'$, and an ester number 31·28, corresponding with 10·95 per cent. of linalyl acetate. A bright yellow oil from *Hyptis spicata* (*Mesophaerum spicatum*; *Labiatæ*), also from Florida, had a sp. gr. 0·915 at 15°, $[\alpha]_D - 27°25'$, acid number 2·17, and ester number 4·35; it probably contained small quantities of menthone or pulegone. A green oil from *Ambrosia artemisiæfolia* had a sp. gr. 0·876 at 15°, $[\alpha]_D - 1°$, and ester number 7·94. A pale yellow oil from *Eupatorium capillifolium* had a sp. gr. 0·926 at 15°, $[\alpha]_D + 18°38'$, and an ester number 7·11. The pale greenish-blue colour of an Australian *essence de Bruyère* was found to be due to the presence of copper; the essence had a sp. gr. 0·8587 at 15° and $[\alpha]_D + 2°44'$. The oil distilled from the wood of *Erythroxylon monogynum* formed a gummy, crystalline mass, which had a pleasant odour. It contained a compound $C_{20}H_{32}O$ of an alcoholic character, which crystallises from light petroleum in needles and melts at 117—118°; the acetate melts at 72—73°. E. W. W.

Essential Oil of Artemisia Herba Alba of Algeria. EMILIEN GRIMAL (*Bull. Soc. chim.*, 1904, [iii], 31, 694—697).—The fresh plant, when steam-distilled previous to the flowering stage, furnishes 0·3 per cent. of a yellowish-green oil with a pleasant, aromatic odour and a camphoraceous, slightly bitter taste. It is readily soluble in 80 per cent. alcohol and less so in 70 and 60 per cent. alcohols, has a sp. gr. 0·9456 at 15°, n_D 1·47274 at 20°, and $[\alpha]_D - 15°30'$ at 20°. The acid number is 6·46, and saponification numbers before and after acetylation 89·23 and 135·38 respectively, corresponding with 24·48 per cent. of combined alcohols and 12·65 per cent. of free alcohols respectively.

The oil distilled between 35° and 135°, and the proportions and principal physical properties of the nine fractions collected are tabulated in the original. The oil is found to contain *l*-camphene, cineol, *l*-camphor, an alcohol, furnishing on oxidation with chromic acid a product having the odour of citral, and esters of octoic and decoic acids. T. A. H.

Essential Oil of Laurel Leaves. HERMANN THOMS and B. MOLLE (*Arch. Pharm.*, 1904, 242, 161—181).—The oil examined amounted to 2·4 kilos. and had sp. gr. 0·9215 at 17°, $\alpha_D - 15·95°$ at 17° in a 100 mm. tube, acid number 2·74, saponification number 49·8. The

free acids consisted of acetic, *iso*butyric, and (*iso*?) valeric. About 1·7 per cent. of free eugenol was present, and about 0·4 per cent. in the form of esters. The acids obtained by hydrolysing the oil with alcoholic potassium hydroxide consisted mainly of acetic acid; the other volatile acids present were probably valeric and hexoic, approximately in the proportion 2 : 3. A monobasic *acid*, $C_{10}H_{14}O_2$, insoluble in water, was also obtained in yield of 0·07 per cent., and its *silver*, *lead*, and *copper* salts were analysed; this acid melts at 146—147°, takes up 2Br, and decolorises permanganate solution energetically in the cold; possibly it has the constitution



and probably it is formed through the action of the potassium hydroxide on the oil. Pinene (compare Wallach, Abstr., 1889, 1072) can no longer be detected in the oil after the treatment with alkali.

The oil remaining after the free acids, phenols, and esters had been removed was fractionated. Cineol, $C_{10}H_{18}O$, was obtained from it in yield equal to 50 per cent. of the original oil; it can be purified by means of the crystalline compound that it forms with arsenic (as with phosphoric) acid; this compound is decomposed by water into its constituents. From the fractions boiling between 212° and 230°, geraniol was isolated; these fractions yielded terpinene when boiled with 50 per cent. sulphuric acid, and terpine hydrate when treated with acid of 5 per cent. strength or more. The fractions of still higher boiling point contain oxygen; probably they contain a sesquiterpene alcohol as well as a sesquiterpene. These fractions, and also the original oil, give an intense blue coloration when they are dissolved in glacial acetic acid and bromine vapour is blown over the surface of the solution. Methylchavicol could not be detected in the oil. C. F. B.

Aucubin. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1904, **138**, 1114—1116. Compare Abstr., 1902, i, 634).—The glucoside aucubin, $C_{13}H_{19}O_8,H_2O$, found together with sucrose, not only in the seeds, but also in the leaves, stem, and root of *Aucuba japonica*, is soluble in water, or ethyl or methyl alcohol, 100 parts of the solvent at 20—22° dissolving 35·6 parts in the case of water, 1·1 parts in the case of 95 per cent. alcohol, 7·7 in the case of 85 per cent. alcohol, and 13·8 in the case of methyl alcohol free from acetone; it is insoluble in ether or chloroform, and crystallises with one molecular proportion of water, which it loses on prolonged heating at 115—120°. Aucubin is readily hydrolysed by very dilute acids, or by a ferment identical with emulsin found in the leaves of the plant forming dextrose and *aucubigenin*, $C_7H_9O_3$, according to the equation

$$C_{13}H_{19}O_8 + H_2O = C_6H_{12}O_6 + C_7H_9O_3.$$

Both aucubin and aucubigenin are without toxic action.

M. A. W.

The Glucoside Robinin. NICOLAI A. WALJASCHKO (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 421—438. Compare Schmidt and Waljaschko, Abstr., 1901, i, 602).—The robinin examined was

obtained from white azaleas (*Robinia pseudacacia L.*), by extracting the flowers either when fresh with water or when dried with alcohol. Its composition is $C_{33}H_{40}O_{19},7\frac{1}{2}H_2O$; $7H_2O$ are lost readily, and the remaining $\frac{1}{2}H_2O$ at 110°. By means of dilute mineral acids, robinin is hydrolysed, yielding galactose (1 mol.), rhamnose (2 mols.), and a yellow colouring matter, to which the author gives the name robigenin: $C_{33}H_{40}O_{19} + 3H_2O = C_6H_{12}O_6 + 2C_6H_{12}O_5 + C_{15}H_{10}O_6$. Robigenin yields crystals, $C_{15}H_{10}O_6,H_2O$, which lose their water at 130° and melt at 270°. T. H. P.

Triphenylmethane Dyes, Stable towards Alkalis. Charles Lauth (*Compt. rend.*, 1904, 138, 1220—1221).—By the action of acetyl chloride, acetic anhydride, or benzenesulphonic chloride on the leuco-bases obtained by reducing the condensation products of *m*-nitrobenzaldehyde and dimethyl- or diethyl-aniline, the hydrogen of the NH_2 group is replaced by an acetyl or benzenesulphonyl radicle, and the resulting compounds on sulphonation and oxidation yield *blue* dyes analogous to *patent blue* in purity of tint and stability towards alkalis, the substituted NH_2 group in the new series of compounds apparently playing the same *rôle* as the hydroxyl in the original series. M. A. W.

Black Sulphur Dye from *m*-Phenylenediamine. Kalle & Co. (D.R.-P. 150834).—A black dye is obtained by fusing *m*-phenylenediamine with *o*-nitrophenol, sodium sulphide, and sulphur, the latter substances being in the proportion to form sodium tetrasulphide. It is not possible to replace the *o*-nitrophenol by *o*-aminophenol. C. H. D.

Lactucon. Friedrich Sperling (*Chem. Centr.*, 1904, i, 1162; from *Zeit. Oesterr. Apoth.-Ver.*, 42, 249—252).—*Lactucon*, $C_{23}H_{36}O_2$, prepared by extracting *Luctucarium germanicum* with light petroleum, is a white, odourless substance which crystallises from hot alcohol in colourless needles and melts at 184°. It is readily soluble in ether, benzene, chloroform, light petroleum, carbon disulphide, or hot alcohol, but very sparingly so in cold alcohol and insoluble in water. By the action of a boiling 1 per cent. solution of potassium hydroxide in alcohol, lactucon yields acetic acid and lactucol. *Lactucol*, $C_{21}H_{33}\cdot OH$, crystallises from alcohol in needles and melts at 154·5°. The bromine *compound*, $C_{23}H_{36}O_2Br_2$, prepared by the action of bromine dissolved in carbon disulphide on lactucol, crystallises in yellow needles and decomposes on heating. Lactucon is the acetyl derivative of lactucol. E. W. W.

Synthesis of Kaempferol. Stanislaus von Kostanecki, Victor Lampe, and Josef Tambor (*Ber.*, 1904, 37, 2096—2099).—When 2′-hydroxy-4′ : 6′ : 4-trimethoxychalkone,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OMe$$

(compare this vol., i, 426), is boiled in alcoholic solution with dilute sulphuric acid, it is converted into 5 : 7 : 4′-*trimethoxyflavanone*,

$$C_6H_2(OMe)_2{<}\begin{matrix} O-CH\cdot C_6H_4\cdot OMe \\ CO\cdot CH_2 \end{matrix},$$

which separates from alcohol in white pyramids and melts at 125°. It forms a yellow solution with alcoholic sodium hydroxide. The iso*nitroso*-derivative, $C_6H_2(OMe)_2<\begin{matrix}O-CH\cdot C_6H_4\cdot OMe\\ CO\cdot C:N\cdot OH\end{matrix}$, prepared by the action of amyl nitrite on the preceding compound, separates from alcohol in pale yellow needles, which melt and decompose at 189—190°. When boiled with dilute sulphuric acid, it forms 5 : 7 : 4′-*trimethoxyflavonol*, $C_6H_2(OMe)_2<\begin{matrix}O-C\cdot C_6H_4\cdot OMe\\ CO\cdot C\cdot OH\end{matrix}$, which crystallises from alcohol in pale yellow needles, grouped in rosettes, and melts at 151—152°. Its *sodium* salt is intensely yellow; its *acetyl* derivative separates from dilute alcohol in white needles and melts at 190—191°. When 5 : 7 : 4′-trimethoxyflavonol is heated with strong hydriodic acid, it forms 5 : 7 : 4′-trihydroxyflavonol (kaempferol),

$$(OH)_2C_6H_2<\begin{matrix}O-C\cdot C_6H_4\cdot OH\\ CO\cdot C\cdot OH\end{matrix}.$$

Acetyl-5 : 7 : 4′-trimethoxyflavonol, when warmed with hydriodic acid, gave 5 : 7 : 4′-trihydroxyflavonol, melting at 275°, whilst Gordin and Kostanecki give 271° as the melting point of naturally occurring kaempferol.

Acetyl-5 : 7 : 4′-triacetoxyflavonol forms prismatic needles and melts at 181°. A. McK.

5 : 7-Dihydroxy-2-methylchromone. E. Jochum and Stanislaus von Kostanecki (*Ber.*, 1904, 37, 2099—2101. Compare Kostanecki and de Wildt, Abstr., 1902, i, 303).—2 : 4 : 6-*Trimethoxy-acetylacetophenone*, $C_6H_2(OMe)_3\cdot CO\cdot CH_2\cdot COMe$, obtained by condensing phloracetophenone dimethyl ether with ethyl acetate by means of sodium, separates from dilute alcohol in colourless prisms and melts at 94—95°; its alcoholic solution gives a red coloration with ferric chloride. When boiled with strong hydriodic acid, it forms 5 : 7-*dihydroxy-2-methylchromone*, $C_6H_2(OH)_2<\begin{matrix}O-CMe\\ CO\cdot CH\end{matrix}$, which separates from alcohol in glistening, tiny plates and melts at 290°. Its solution in concentrated sulphuric acid is colourless and does not exhibit fluorescence. Its *acetyl* derivative separates from dilute alcohol in white needles and melts at 149°. A. McK.

Synthesis of 6 : 2′-Dihydroxyflavonol. A. Katschalowsky and Stanislaus von Kostanecki (*Ber.*, 1904, 37, 2346—2351).—The tinctorial properties of 6 : 2′-dihydroxyflavonol are contrasted with those of 6 : 3′-dihydroxyflavonol (this vol., i, 441) and 6 : 4′-dihydroxyflavonol (this vol., i, 442). With respect to the theory of dyes, the 2′ : 3-position in the flavone group is comparable with the peri-position in the naphthalene series, and is designated by the authors as the *anchi*-position.

6 : 2′-*Dimethoxyflavanone*, $OMe\cdot C_6H_3<\begin{matrix}O-CH\cdot C_6H_4\cdot OMe\\ CO\cdot CH_2\end{matrix}$, prepared by adding sodium hydroxide to an alcoholic solution of quinacetophenone monomethyl ether (this vol., i, 440) and salicylaldehyde

methyl ether, forms colourless pyramids and melts at 120°; its solution in concentrated sulphuric acid is red. The iso*nitroso*-derivative, $OMe\cdot C_6H_3<\begin{matrix}O-CH\cdot C_6H_4\cdot OMe\\ CO\cdot C:N\cdot OH\end{matrix}$, prepared by the action of amyl nitrite on the preceding compound, separates from alcohol in yellow needles and melts and decomposes at 164—166°.

6 : 2′-*Dimethoxyflavonol*, $OMe\cdot C_6H_3<\begin{matrix}O-C\cdot C_6H_4\cdot OMe\\ CO\cdot C\cdot OH\end{matrix}$, prepared by hydrolysis of the preceding oxime with sulphuric acid, separates from alcohol in colourless prisms and melts at 187—188°; it is insoluble in cold sodium hydroxide, but on warming it dissolves to a yellow solution, from which the yellow sodium salt separates on cooling. The *acetyl* derivative separates from dilute alcohol in colourless, prismatic needles and melts at 121—122°.

6 : 2′-*Dihydroxyflavonol*, $OH\cdot C_6H_3<\begin{matrix}O-C\cdot C_6H_4\cdot OH\\ CO\cdot C\cdot OH\end{matrix}$, prepared by the action of hydriodic acid on the dimethyl ether, crystallises from dilute alcohol in pale yellow needles and melts at 242—243°. It is easily soluble in dilute sodium hydroxide. A. McK.

3-Alkyl-substituted Benzopyranols. Carl Bülow and Ivo Deiglmayr (*Ber.*, 1904, **37**, 1791—1800. Compare Bülow, Abstr., 1903, i, 272).—Further evidence is now submitted to prove that the condensation product formed from methylacetylacetone and resorcinol is 7-hydroxy-2 : 3-dimethyl-4-methylene-1 : 4-benzopyranol. The general nature of the reaction is also indicated by the substitution of orcinol (1 : 3 : 4-trihydroxybenzene), pyrogallol, and phloroglucinol respectively for resorcinol (*m*-dihydroxybenzene).

7-*Hydroxy*-2 : 3-*dimethyl*-4-*methylene*-1 : 4-*benzopyranol*, prepared by adding an excess of sodium acetate to the hydrochloride previously described (*loc. cit.*), separates from dilute alcohol in microscopic, brick-red crystals; it forms, with concentrated sulphuric acid, a yellow solution, which, when diluted, exhibits bluish-violet fluorescence. Its *acetyl* derivative is amorphous. The constitution of 7-hydroxy-2 : 3-dimethyl-4-methylene-1 : 4-benzopyranol was proved by the isolation of methyl ethyl ketone, resacetophenone, resorcinol, and acetic acid as products resulting from the action of a concentrated aqueous solution of potassium hydroxide on the hydrochloride.

7-*Hydroxy*-2 : 3 : 5-*trimethyl*-4-*methylene*-1 : 4-*benzopyranol hydrochloride*, prepared by condensing methylacetylacetone with orcinol, forms lemon-yellow needles, which melt and decompose at 192—196°. With sulphuric acid, it forms a yellow solution which exhibits a faint blue fluorescence. The corresponding *picrate* melts and decomposes at 180—185°.

6 : 7-*Dihydroxy*-2 : 3-*dimethyl*-4-*methylene*-1 : 4-*benzopyranol hydrochloride*, prepared from methylacetylacetone and 1 : 3 : 4-trihydroxybenzene, separates from dilute hydrochloric acid in bright yellow, silky needles which crystallise with $2\frac{1}{2}H_2O$ and 1HCl; it melts and decomposes at 255—265°, and its solutions are feebly fluorescent. The corresponding *picrate* was also prepared.

7 : 8-*Dihydroxy*-2 : 3-*dimethyl*-4-*methylene*-1 : 4-*benzopyranol hydrochloride*, prepared from methylacetylacetone and pyrogallol, crystallises with $1H_2O$ and forms orange-red needles, which, with concentrated sulphuric acid, form a lemon-yellow solution, with sodium hydroxide a bluish-black solution, and with ammonia a carmine-red solution. The corresponding *picrate* melts and decomposes at 195—200°. The free *base* forms a dark carmine-red powder; its *diacetyl* derivative softens at 135° and melts completely at 148°.

5 : 7-*Dihydroxy*-2 : 3-*dimethyl*-4-*methylene*-1 : 4-*benzopyranol hydrochloride*, prepared from methylacetylacetone and phloroglucinol, crystallises with 1HCl and $1H_2O$. It forms fine, brownish-yellow needles. Its solution in concentrated sulphuric acid is bright yellow. The corresponding *picrate* was also prepared. The free *base* is a yellow, amorphous powder; its *diacetyl* derivative is a green, amorphous powder. A. McK.

New Condensation Derivatives of Benzoylphthalylacetone. CARL BÜLOW [with BERTHOLD KOCH] (*Ber.*, 1904, 37, 1964—1971).—3-*Benzoyl*-7-*hydroxy*-4-*methylene*-1 : 4-*benzopyranol*-2-*phenyl*-o-*carboxylic acid*, $\begin{array}{l} \mathrm{OH{\cdot}C{:}CH{-}C{\cdot}O{-\!-\!-}C{\cdot}C_6H_4{\cdot}CO_2H} \\ \mathrm{CH{\cdot}CH{\cdot}C{\cdot}C({:}CH_2){\cdot}C{\cdot}COPh} \end{array}$, obtained by passing dry hydrogen chloride through a cold solution of phthalylbenzoylacetone and resorcinol in glacial acetic acid, separates from the solvent in microscopic, golden crystals and melts at 245°; on acetylation, it gives the corresponding 7-*acetoxy*-derivative, $C_{26}H_{18}O_6$, which forms slender, white needles and melts at 148°. When the carboxylic acid is heated with 10 per cent. aqueous potassium hydroxide, it gives acetophenone, resorcinol, phthalic acid, and resacetophenone; it is probable that resacetophenone and benzoylphthalylmethane are the primary products and that they undergo further decomposition.

3-*Benzoyl*-5 : 7-*dihydroxy*-4-*methylene*-1 : 4-*benzopyranol*-2-*phenyl*-o-*carboxylic acid*, $C_{24}H_{16}O_6$, prepared by condensing benzoylphthalylacetone with phloroglucinol, crystallises from glacial acetic acid and melts and decomposes at 263°; its *diacetyl* derivative, $C_{28}H_{20}O_8$, melts and decomposes at 189°.

Alternative formulæ for the foregoing pyranol derivatives are suggested and the mechanism of the condensation discussed.

W. A. D.

The Indophenine Reaction. LUDWIG STORCH (*Ber.*, 1904, 37, 1961).—The indophenine reaction, although not given by isatin with benzene containing thiophen in presence of pure sulphuric acid, is at once produced on gently warming the mixture; that the addition of a solution of ferric chloride or potassium dichromate simply develops the heat necessary for the interaction is shown by the fact that water produces the same effect (compare Bauer, this vol., i, 519).

W. A. D.

Condensation Products from Thalline and Cotarnine. CARL RENZ and MARTIN HOFFMANN (*Ber.*, 1904, 37, 1962—1964).—Thalline condenses with phthalic anhydride (1 mol.) with elimination of H_2O to form a *compound*, $C_{18}H_{15}O_3N$, which, after being boiled with alcohol

and recrystallised from glacial acetic acid, separates in white, lustrous crystals melting at 239° and having the composition

$$2C_{18}H_{15}O_3N,C_2H_6O.$$

Cotarnine, on being heated with vanillin at 100—110°, gives a *product*, the *hydrochloride*, $C_{10}H_{17}O_4N,HCl,H_2O$, of which, crystallises from alcohol in golden-coloured needles and melts at 198°; the corresponding base could not be obtained. With catechuic aldehyde, cotarnine condenses giving a *base*, the *hydrochloride*, $C_{19}H_{19}O_6N,HCl$, of which melts at 159—160°. W. A. D.

Conversion of Papaverine into an *iso*Quinoline Base derived from Phenanthrene.

ROBERT PSCHORR [with M. STÄHLIN and M. SILBERBACH] (*Ber.*, 1904, 37, 1926—1942).—Hesse's nitropapaverine (*Annalen*, 1872, Suppl. 8, 292) is proved to contain the nitro-group in the ortho-position to the CH_2 group,

$$NO_2{\cdot}C_6H_2(OMe)_2{\cdot}CH_2{\cdot}C_9NH_3(OMe)_2.$$

It crystallises from ethyl acetate in long, colourless needles, becoming yellow in air, melts at 186—187° (corr.), and dissolves in 100—110 parts of boiling alcohol, 40 parts of ethyl acetate, 3 parts of chloroform, or 10 parts of xylene. The *methiodide*, $C_{21}H_{23}O_6N_2I$, crystallises from water in thick, yellow prisms, melts at 225° (corr.), and decomposes at 235°; the *methobromide* forms bright yellow prisms, darkening at 210° and melting and decomposing at 227° (corr.). The *methomethyl sulphate* forms bright yellow prisms and melts and decomposes at 238° (corr.), and reacts with potassium chloride to form the *methochloride* melting at 212° (corr.).

Potassium permanganate oxidises nitropapaverine methiodide to 6-nitroveratric acid (6-nitro-3:4-dimethoxybenzene-1-carboxylic acid). Boiling potassium hydroxide forms 6-nitrohomoveratrole (6-nitro-3:4-dimethoxy-1-methylbenzene) and *dimethoxy*iso*quinolone*, $C_{12}H_{13}O_3N$, which crystallises from benzene in thick, colourless prisms, sinters at 102°, and melts at 107°; its *hydrochloride* forms silky needles and melts at 186—187° (corr.).

Stannous chloride reduces nitropapaverine to *aminopapaverine*, forming slender, felted needles containing alcohol and melting at 116°; after removal of the alcohol by heating or prolonged drying, it sinters at 130° and melts at 143° (corr.). The *acetyl* derivative crystallises with 1 mol. of benzene and melts at 125°; when dried, it melts at 162° (corr.).

Diazopapaverine, $C_{20}H_{19}O_4N_3$, prepared by adding sodium nitrite to a solution of aminopapaverine in cold concentrated sulphuric acid, crystallises from alcohol in colourless tablets and melts at 281° (corr.). The *methiodide*, $C_{21}H_{22}O_4N_3I,H_2O$, forms slender, yellow needles, and after drying sinters at 185° and melts and decomposes at 198° (corr.). The *methomethyl sulphate* forms star-shaped groups of yellow needles, sinters at 163°, and melts at 168—169° (corr.). Potassium hydroxide converts diazopapaverine methiodide into an orange compound, melting at 170°, dissolving readily in water, and containing no iodine (compare Decker and Klauser, this vol., i, 338).

Nitropapaveraldine, prepared by heating papaveraldine (Goldschmidt, Abstr., 1886, 478) with nitric acid, crystallises from alcohol in slender, yellow needles and melts at 199—200° (corr.). The same compound is

obtained on oxidising nitropapaverine in boiling glacial acetic acid solution with sodium dichromate. Stannous chloride reduces it, forming a mixture of anthranilopapaverine and aminopapaveraldine. *Anthranilopapaverine*, $C_{20}H_{18}O_5N_2$, crystallises from alcohol in slightly yellow, slender needles, sinters at 235° and melts at 244—245° (corr.). It dissolves readily in chloroform, very sparingly in alcohol, acetone, or ethyl acetate, and is insoluble in water or ether. It is probably an internal anhydride resembling methylanthranil and containing the group $:\mathrm{C}\overset{\mathrm{O}}{\frown}\mathrm{N}$. Concentrated sulphuric acid converts it into a *sulphonic acid* melting at 233°.

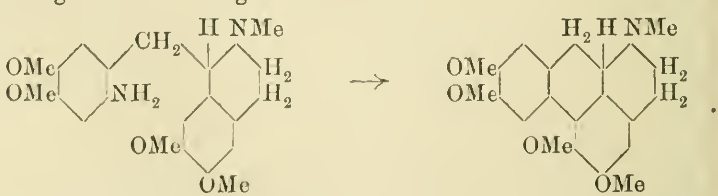
Aminopapaveraldine, $C_{20}H_{20}O_5N_2$, obtained from the filtrate from the above compound, or by reducing nitropapaveraldine with ammonium sulphide, crystallises from alcohol in bright yellow needles and melts at 171—172° (corr.), dissolving readily in organic solvents, sparingly in hot water. Dilute acids dissolve it to intensely red solutions, concentrated acids form bright yellowish-green solutions, becoming red on dilution.

Diazopapaveraldine sulphate, $C_{20}H_{19}O_9N_3S$, crystallises from warm water in microscopic, orange needles, darkens at 120°, and melts at 225° (corr.) to a dark green liquid.

Amino-N-methyltetrahydropapaverine, $C_{21}H_{28}O_4N_2$, prepared by reducing nitropapaverine methochloride with tin and hydrochloric acid, crystallises from ethyl acetate or methyl alcohol in stellar groups of needles, melts at 145° (corr.), and dissolves readily in chloroform, very sparingly in ether. The hydrochloride, sulphate, and nitrate dissolve readily in water, slightly acid solutions give an intense, permanent, blue coloration with ferric chloride. The base may be regarded as *dl*-aminolaudanosine (compare Pictet and Athanasescu, Abstr., 1900, i, 685).

When a smaller quantity of hydrochloric acid is employed in the reduction, *aminopapaverine methochloride hydrochloride*, $C_{21}H_{26}O_4N_2Cl_2$, is obtained, crystallising in colourless tablets and melting at 200° (corr.). *Aminopapaverine methochloride* forms slightly yellow needles and melts at 147° (corr.).

When copper powder is added to a diazotised solution of *N*-methyltetrahydroaminopapaverine, a syrupy liquid is obtained, from which crystals of *phenanthreno-N-methyltetrahydropapaverine methiodide*, $C_{22}H_{28}O_4NI$, are obtained by adding methyl iodide and extracting with acetone. The methiodide crystallises from alcohol in faintly yellow prisms and melts at 215° (corr.). Its formation takes place according to the following scheme:



C. H. D.

Lupinidine and Sparteine. RICHARD WILLSTÄTTER and WILHELM MARX (*Ber.*, 1904, 37, 2351—2357).—Willstätter and Fourneau have shown (Abstr., 1902, i, 557) that lupinine and lupinidine are not identical, the latter having the high boiling point 311—314°, and that lupinidine resembles sparteine in many properties.

Lupinidine, $C_{15}H_{26}N_2$, was prepared from the seeds of *Lupinus luteus*, the amount obtained after removal of lupinine by treatment with light petroleum being 0·23 per cent. of the seeds used. It boils at 180·5° under 18 mm. pressure and has the sp. gr. 1·034 at 0° and 1·023 at 20°. The data in the literature respecting the boiling point of sparteine are discordant; according to Peratoner, sparteine boils at 185—190° under 18 mm. pressure. The authors find for lupinidine $[\alpha]_D$ $-5·96°$ at 20° and $[\alpha]_D$ $-16·41°$ at 21° in 99 per cent. alcohol, where $c = 14·206$; whilst, according to Moureu and Valeur (Abstr., 1903, i, 717), the corresponding values for sparteine are $-5·41°$ and $-16·42°$ ($c = 10—15$). Lupinidine and sparteine also possess identical solubilities, since when their aqueous solutions, saturated at 18°, are precipitated by picric acid, the amounts precipitated from the respective solutions being practically identical. The platinichlorides of sparteine and lupinidine are identical; both begin to blacken at 239°, and melt with decomposition at 243·5°. *Sparteine hydrogen sulphate* separates in prisms, which melt and decompose at 232°. A. McK.

Cevadine [Veratrine]. II. MARTIN FREUND [and EDMUND SPEYER] (*Ber.*, 1904, 37, 1946—1957. Compare Freund and Schwarz, Abstr., 1899, i, 464).—Only one acyl group can be introduced into veratrine; cevine, on the other hand, allows of the introduction of two acyl groups.

Benzoylveratrine benzoate, $C_{32}H_{48}O_9NBz,C_6H_5{\cdot}CO_2H,H_2O$, prepared by heating veratrine with benzoic anhydride at 105—107°, crystallises from dilute alcohol in small, white needles, becomes anhydrous at 120°, and melts at 150—155°. It dissolves readily in alcohol, benzene, or acetone, sparingly in ether, very slightly in water. *Benzoylveratrine*, precipitated by ammonia from the alcoholic solution of the benzoate, crystallises from alcohol in small, triangular prisms and melts at 255°. The *hydrochloride*, $C_{39}H_{53}O_{10}N,HCl,H_2O$, forms small, white needles; the *hydriodide* forms yellowish-white needles and melts at 220—222°; the *nitrate* forms small, white needles and melts at 194—195°.

Acetylveratrine, $C_{32}H_{48}O_9NAc$, melts at 182° to a viscous mass, then solidifies, and again melts at 234° to a yellow liquid The *hydrochloride* is a brittle mass dissolving readily in water.

Dibenzoylcevine benzoate, $C_{41}H_{51}O_{10}N,C_6H_5{\cdot}CO_2H$, forms microscopic prisms and melts at 193—195°. Ammonia precipitates *dibenzoylcevine*, crystallising in large tablets and melting at 195—196°. The *hydrochloride* forms small, prismatic tablets containing H_2O, sinters at 223° and melts at 227°. The *nitrate* forms small rods and melts at about 262°; the amorphous *acetate* melts at 170°.

Diacetylcevine melts at 190°.

Hydrogen peroxide oxidises cevine to *cevine oxide*, $C_{27}H_{43}O_9N$, crystallising from dilute alcohol in white rods and melting at 275—278°. The *hydrochloride* is amorphous and decomposes at about 208—210°.

On the addition of alkali to the solution, the base is not obtained until after warming, when it separates in a pure state. The *aurichloride* is amorphous and melts and decomposes at 185°. Sulphur dioxide in chloroform solution reduces cevine oxide to a *compound*, $C_{27}H_{43}O_8 \vdots N \Big< {}^{O}_{SO_2}$ (compare Wolffenstein, Abstr., 1899, i, 495). Barium chloride reconverts this into cevine. The formation of the oxide indicates that cevine is a tertiary base, and probably contains a double ring-system, as in the case of hydroberberine.

The physiological action of the compounds described is set forth in detail by Heinz. C. H. D.

Action of Sulphuryl Chloride on Pyrrole. IV. GIROLAMO MAZZARA and A. BORGO (*Gazzetta,* 1904, 34, i, 253—262. Compare Abstr., 1902, i, 820; 1903, i, 51 and 274).—2 : 3 : 5-*Trichloropyrrole,* $C_4NH_2Cl_3$, prepared by gradually adding sulphuryl chloride ($3\frac{1}{2}$ mols.) to an ethereal solution of pyrrole (1 mol.), kept cool by means of ice, is obtained as a pale yellow oil which could not be purified ; it blackens under the action of light and its vapours irritate the eyes. On treatment, in methyl-alcoholic solution, with methyl iodide and potassium hydroxide, it yields 2 : 3 ; 5-*trichloro*-1-*methylpyrrole,* $C_4NHMeCl_3$, which is a colourless oil, heavier than water ; it darkens but little in the light and its vapour attacks the eyes.

Chloromaleic methylimide, $NMe\Big<\begin{matrix}CO\cdot CH\\ \Vert\\ CO\cdot CCl\end{matrix}$, prepared by oxidising 2 : 3 : 5-trichloro-1-methylpyrrole by means of concentrated nitric acid, crystallises from light petroleum in white, nacreous plates melting at 79° ; it is volatile in a current of steam, and its vapour has a very pungent odour and strongly attacks the eyes.

2 : 3 : 4 : 5-*Tetrachloro*-1-*methylpyrrole,* C_4NMeCl_4, prepared from the tetrachloropyrrole obtained in small quantity by the action of $3\frac{1}{2}$ mols. of sulphuryl chloride on 1 mol. of pyrrole, crystallises from light petroleum in short, stout needles, which melt at 118—119° and dissolve in concentrated sulphuric acid yielding a pale rose-coloured solution. On oxidation with concentrated nitric acid, this compound yields *dichloromaleic methylimide,* $NMe\Big<\begin{matrix}CO\cdot CCl\\ \Vert\\ CO\cdot CCl\end{matrix}$, which separates from alcohol in large, shining plates melting at 86° ; it is volatile in a current of steam and its vapour irritates the eyes.

T. H. P.

Action of Hydrazine on Ethyl αβ-Diacetylpropionate (Ethyl 2 : 5-Hexadione-3 carboxylate). G. KORSCHUN (*Ber.,* 1904, 37, 2183—2192).—Ethyl 2 : 5-hexadione-3-carboxylate reacts vigorously with hydrazine in alcoholic solution, forming ethyl 3 : 6-dimethyl-4 : 5-dihydropyridazine-4-carboxylate and ethyl 3 : 6-dimethylpyridazine-4-carboxylate, which have been obtained by Bülow (Abstr., 1903, i, 196) and Paal and Ubber (Abstr., 1903, i, 290) from the dicarboxylate. *Ethyl* 2 : 5-*dimethylfuran*-3-*carboxylate,* $C_9H_{12}O_3$, is produced at the same time, but is not readily obtained pure. It is identified by hydrolysis to the corresponding acid.

An ester of high boiling point is also produced, and is possibly ethyl 1-bis-2 : 5-dimethylpyrrole-3-carboxylate. The acid obtained by hydrolysis is crystalline and melts and decomposes above 360°.

Hydrazine acetate reacts with ethyl hexadionecarboxylate to form *ethyl* 2 : 5-*dimethylpyrrole-3-carboxylate*, $C_9H_{14}O_2N_2$, which crystallises from hot water and melts at 87—88°, and dissolves readily in organic solvents. It is not hydrolysed by boiling with alcoholic potassium hydroxide, and does not yield benzoyl or acetyl derivatives.

C. H. D.

Action of Phenylhydrazine on Ethyl αβ-Diacetylpropionate (Ethyl 2 : 5-Hexadione-3-carboxylate). G. Korschun (*Ber.*, 1904, 37, 2192—2195. Compare Borsche and Spannagel, *Annalen*, 1904, 331, 315).—Phenylhydrazine converts ethyl 2 : 5-hexadione-3-carboxylate in ethereal solution into the *diphenylhydrazone*,

$$NHPh\cdot N{:}CMe\cdot CH_2\cdot CH(CO_2Et)\cdot CMe{:}N\cdot NHPh,$$

which crystallises from alcohol and decomposes at 130°.

When only 1 mol. of phenylhydrazine is employed in alcoholic solution, no monophenylhydrazone is obtained, but the diphenylhydrazone is formed together with the ester of an *acid*, $C_{13}H_{14}O_2N_2$, which crystallises from alcohol and melts and decomposes at 210° when rapidly heated. The same acid is produced in larger quantity when phenylhydrazine acetate reacts with the keto-ester. C. H. D.

Synthesis of Methyl 2 : 5-Dimethylpyrrole-3-carboxylate. G. Korschun (*Ber.*, 1904, 37, 2196—2197).—*Methyl* 2 : 5-*dimethylpyrrole-3-carboxylate*, prepared from methyl acetoacetate, chloroacetone, and dilute ammonia in the manner employed by Hantzsch (Abstr., 1890, 1155) for the preparation of the ethyl ester, crystallises from dilute alcohol and melts at 119·5° and boils at 170° under 15 mm. pressure.

The reaction was explained by Hantzsch as being due to the intermediate formation of ethyl β-aminocrotonate. It is not, however, possible to prepare the ester directly from ethyl β-aminocrotonate and chloroacetone, and the reaction is better explained by the formation of an ester of diacetopropionic acid, which then condenses with ammonia to form the pyrrole derivative. C. H. D.

Pyridine Bases in Brown-coal Tar. Krey (*Zeit. angew. Chem.*, 1904, 17, 624).—The author proved, in 1887, that pyridine bases occur in brown-coal tar. A. McK.

Bases from Coal Tar. Felix B. Ahrens and Richard Gorkow (*Ber.*, 1904, 37, 2062—2066. Compare Abstr., 1895, i, 390; 1897, i, 203; 1903, i, 515).—2 : 5-Dimethylpyridine has been isolated from a fraction of coal tar boiling at 160—165° by means of its *mercurichloride* derivative, $C_7H_9N,HCl,6HgCl_2$, which melts at 162—164°. The base distils at 159—160° (corr.); the *aurichloride* forms golden-yellow crystals, the *platinichloride*,

$$(C_7H_9N)_2H_2PtCl_6,2H_2O,$$

brick-red crystals melting at 192—194°, and the *picrate* yellow needles melting at 156—157°. On oxidation with 2 per cent. permanganate

it yields an acid melting at 244° and giving a red coloration with ferrous sulphate solution. When this acid is heated at 250°, it loses carbon dioxide and yields *iso*cinchomeronic acid. 2 : 5-Dimethylpiperidine, purified by the acid of its nitrosoamine, forms a clear liquid, distilling at 138—140° (corr.). The *hydrochloride* crystallises in well-developed needles melting at 194—195°. The *hydrobromide* melts at 148—149°, the *hydriodide* at 167—168°, the *platinichloride* at 210°, and the *aurichloride* at about 80°.

A fraction of coal tar boiling at 165—170° gave a *mercurichloride* melting at 172—173°, which, on decomposition with potassium hydroxide, gave 3 : 5-dimethylpyridine, boiling at 171° (corr.). The *platinichloride* crystallises in quadratic plates melting at 254—255°, the *aurichloride* melts at 146—147°, and the *picrate* at 228—230°. The base on oxidation yields pyridine-2 : 4-dicarboxylic acid.

2 : 4-Dimethylpyridine yields a *hydrochloride*, which is hygroscopic and melts at 195—197°. The *hydrobromide* melts at 189—190° and the *aurichloride* at 75°.

1-*Amino*-2 : 4-*dimethylpiperidine*, $C_5H_8Me_2N\cdot NH_2$, obtained by the electrolytic reduction of a 50 per cent. sulphuric acid solution of nitroso-2 : 4-dimethylpiperidine, is a liquid distilling at 170—175°.

J. J. S.

Derivatives of 2-Picolyl- and 2-Picolylmethyl-alkines. II. Coniceines. KARL LÖFFLER (*Ber.*, 1904, 37, 1879—1899. Compare this vol., i, 265).—The constitution of the four isomeric coniceines obtained by Hofmann (Abstr., 1885, 401) and Lellmann (Abstr., 1890, 1328) has not yet been determined. Their relation to 2-pipecolylmethylalkines has been shown by Ladenburg (Abstr., 1890, 67).

Fuming hydrobromic acid and red phosphorus at 125° convert 2-pipecolylalkine into a *bromide*, $C_7H_{14}NBr$, which decomposes on distillation. The *hydrochloride*, $C_5NH_{10}\cdot C_2H_4Br,HCl$, forms small, hygroscopic needles and melts at 148°. The iodo-base is prepared in similar manner and forms a *hydriodide*, $C_7H_{14}NI,HI$, melting at 162—163°, which by moist silver chloride is converted into the *hydrochloride* of the chloro-base, sintering at 148° and melting at 149·5°. The *aurichloride*, $C_7H_{14}NCl,HAuCl_4$, forms microscopic crystals and melts at 110·5°. Bases resembling coniceine could not be prepared by heating the salts with sodium hydroxide.

Hydriodic acid and red phosphorus at 140° convert 2-pipecolylmethylalkine (Ladenburg, Abstr., 1898, i, 687) into a mixture of two oily bases, the *hydriodides* of which melt at 161° and 163° respectively. When heated with concentrated sodium hydroxide in a sealed tube at 100°, volatile bases are produced.

Base I, from the hydriodide melting at 163°, is a colourless, volatile liquid, fuming strongly with hydrogen chloride. It has the properties of a saturated tertiary base, $C_8H_{15}N$. Its boiling point and the properties of its salts agree with those of ε-coniceine, prepared by Hofmann and Lellman from iodoconine (*loc. cit.*). The *methiodide* forms a white powder and melts at 185—186°, the *ethiodide* forms colourless crystals and melts at 176—177°; its solution in

hydrochloric acid forms a *platinichloride*, $(C_8H_{15}N,EtCl)_2PtCl_4$, crystallising in needles and melting and decomposing at 198—200°.

The base II, $C_8H_{15}N$, from the hydriodide melting at 161°, boils at 158—161°, but was not obtained in sufficient quantity for complete characterisation. The aurichloride melts at 183—184°, and the picrate melts and decomposes at 222°. It is probably the inactive form of α-coniceine, and identical with the coniceine obtained by the action of fuming hydrochloric acid on pipecolylmethylalkine, with which it corresponds in all the properties examined.

Active α-coniceine, prepared by the action of fuming hydrochloric acid on conhydrine, has $[\alpha]_D + 18{\cdot}4°$. The *mercurichloride*,

$$C_8H_{15}N,HCl,6HgCl_2,$$

melts and decomposes at 220—221°; the *ethiodide* melts at 170—171° and forms the chloride with moist silver chloride. The *platinichloride* of the ethyl chloride, $(C_8H_{15}N,EtCl)_2PtCl_4$, decomposes at 208—210°.

The inactive form, prepared from pipecolylmethylalkine, forms similar salts and must have the constitution $\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH{\cdot}CH_2 \\ | \qquad\qquad\quad | \qquad | \\ CH_2{\cdot}CH_2{\cdot}N{-}{-}CHMe \end{array}$, being stereoisomeric with the coniceine prepared from pipecolylmethylalkine iodide. C. H. D.

Derivatives of Quinolinic Acid. BRUNO FELS (*Ber.*, 1904, 37, 2129—2137).—The *potassium* derivative of the imide of quinolinic acid, $C_5H_3N{<}^{CO}_{CO}{>}NK$, prepared by bringing the imide (Philips, Abstr., 1895, i, 572) and potassium together in alcoholic solution, forms a colourless mass of glistening platelets. When heated with ethyl chloro- or bromo-acetate, *ethyl quinolinylglycinate*,

$$C_5H_3N{<}^{CO}_{CO}{>}N{\cdot}CH_2{\cdot}CO_2Et,$$

is formed; this crystallises in glistening, cream-coloured plates, sinters at 120°, and melts at 122°. *Methyl dihydroxyquinopyrine carboxylate*, $C_5H_3N{<}\begin{array}{l} CO{\cdot}NH \\ \quad\;\; | \\ CO{\cdot}CH{\cdot}CO_2Me \end{array}$, is prepared from the foregoing compound on heating it with sodium methoxide; it crystallises in long, flat, silver-grey needles, and on heating becomes coloured at 180°, strongly so at 200°, and melts and decomposes at 203—205°. On boiling with hydrogen iodide, *dioxyquinopyrine*, $C_5H_3N{<}\begin{array}{l} CO{\cdot}NH \\ \quad\;\; | \\ CO{\cdot}CH_2 \end{array}$, is formed, crystallising in yellow needles, which, on heating, become brown at 225° and still darker at 245° without melting. The base is easily soluble in dilute acids and alkali hydroxides, giving pale to brownish-yellow solutions; the *hydrochloride* forms chrome-yellow needles, the *hydriodide* glistening, bright orange prisms, the *aurichloride* reddish-yellow bunches of needles, the *platinichloride* characteristic mahogany-brown crystals shaped like an ear of corn; whilst the *picrate* crystallises in flat, lustrous, golden-yellow needles, which sinter at 202° and melt and decompose at 205°. Dioxyquinopyrine is very easily oxidised by the atmospheric oxygen, and cannot therefore be recrystallised from water; on oxidation with hydrogen peroxide in aqueous ammonia, a

substance is formed giving a bright red, crystalline hydrochloride the composition of which is not yet satisfactorily determined.

E. F. A.

Derivatives of Cinchomeronic Acid. BRUNO FELS (*Ber.*, 1904, 37, 2137—2149).—*Benzylidenemeride*, $C_5NH_3{<}{\overset{\text{—CO—}}{\text{C(CHPh)}}}{>}O$, produced by condensing cinchomeronic anhydride with phenylacetic acid, forms colourless, stellate crystals melting at 178—180°; by the action of sodium methoxide, it is converted into 1 : 3-*diketo*-2-*phenylhydro*-6-*pyrinden*, $C_5H_3N{<}{\overset{CO}{CO}}{>}CHPh$, which crystallises in dark bluish-violet needles and forms a brilliant red-coloured *hydrochloride*. The *barium* derivative, and the *silver* derivative crystallise in carmine-red needles. 4-*Phenylacetylpyridine*-3-*carboxylic acid*, $CH_2Ph{\cdot}CO{\cdot}C_5NH_3{\cdot}CO_2H$, is produced on warming benzylidenemeride with strong alkali hydroxide, and crystallises in well-formed, colourless, rhombic plates melting at 187—188°; the citron-yellow prisms of the *hydrochloride* melt and decompose at 225—260°. The corresponding *amide*, which is formed on heating benzylidenemeride with alcoholic ammonia under pressure, crystallises in colourless, glistening prisms which sinter at 203° and melt at 205—206°.

Benzylidenemerimidine, $C_5NH_3{<}{\overset{\text{—CO—}}{\text{C(CHPh)}}}{>}NH$, crystallises from chloroform in colourless plates, melting at 234—236°. On reducing it with hydrogen iodide and phosphorus, 4-*phenylethylpyridine*-3-*carboxylic acid*, $CH_2Ph{\cdot}CH_2{\cdot}C_5NH_3{\cdot}CO_2H$, is formed; this melts at 156—157° and forms a *picrate* crystallising in canary-yellow needles, which sinter at 154° and melt at 166—167°. On dry distillation with lime, 4-*phenylethylpyridine* is formed; this melts at 69—71° and gives a *platinichloride* melting and decomposing at 214—215°, a *picrate* melting at 162—163°, and an *aurichloride* melting at 183—185° when heated quickly. On oxidation with permanganate, *iso*nicotinic acid is formed.

E. F. A.

Behaviour of 2-Methyltetrahydro*iso*quinoline towards Chromic Acid. MARTIN FREUND and HEINRICH BECK (*Ber.*, 1904, 37, 1942—1946. Compare Beckett and Wright, Trans., 1876, 28, 577, and Freund and Will, Abstr., 1887, 1057).—Unlike hydrocotarnine and hydrohydrastinine, which yield cotarnine and hydrastinine respectively, the nearly-related 2-methyltetrahydro*iso*quinoline (Wedekind and Oechslen, Abstr., 1902, i, 118) does not yield an aldehydic product on oxidation with chromic acid, but forms 1 : 3 : 4-*triketo*-2-*methyltetrahydro*iso*quinoline*, $C_6H_4{<}{\overset{CO\cdot NMe}{\underset{CO\cdot CO}{|}}}$, crystallising from alcohol in yellow needles and melting at 186—187°. The *mono-oxime*, $C_{10}H_8O_3N_2$, melts at 207—208°.

Potassium permanganate oxidises the triketone in alkaline solution to the *methylimide* of phthalic acid, $C_9H_7O_2N$, melting at 133—134°

and dissolving sparingly in water. The same compound was prepared by heating methylamine phthalate.

Concentrated potassium hydroxide decomposes the triketone on boiling, methylamine being evolved. The residue contains a *compound*, $C_{15}H_{12}O_7$, which crystallises from hot water and melts at 199°, and forms crystalline barium and silver salts. C. H. D.

isoCarbostyril Derivatives containing a Meta-substituted Benzene Nucleus. HERRMANN KUSEL (*Ber.*, 1904, 37, 1971—1979).—4-*Ethoxyphthalylglycine*, $OEt\cdot C_6H_3{<}{\substack{CO\\CO}}{>}N\cdot CH_2\cdot CO_2H$, prepared by heating 4-ethoxyphthalic anhydride with glycine at 140°, crystallises from water in flat needles and melts at 179°; the *ethyl* ester,

$$OEt\cdot C_6H_3{:}(CO)_2{:}N\cdot CH_2\cdot CO_2Et,$$

crystallises from alcohol in large, colourless needles, melts at 118°, and, on being heated with alcoholic sodium ethoxide for 3 hours at 100°, gives *ethyl* 4-*hydroxy*-6-(or 7)-*ethoxy*iso*carbostyril*-3-*carboxylate*, $OEt\cdot C_6H_3{<}{\substack{CO\text{——}NH\\C(OH){:}C\cdot CO_2Et}}$. This crystallises from alcohol or water in colourless needles, melts and decomposes at 233°, and, on hydrolysis with hydrobromic or hydriodic acid, gives 1 : 4 : 6- or 1 : 4 : 7-*trihydroxy*-iso*quinoline*, $OH\cdot C_6H_3{<}{\substack{CO\cdot NH\\CO\cdot CH_2}}$ or $OH\cdot C_6H_3{<}{\substack{C(OH){:}N\\C(OH){:}CH}}$, which crystallises from water in needles and does not melt at 300°; by reduction with hydriodic acid and red phosphorus, 1 : 6- or 1 : 7-*dihydroxy*-iso*quinoline* is obtained. It crystallises from water in colourless needles, melts at 270°, and is converted by phosphorus oxychloride into 1 : 6- or 1 : 7-*dichloro*iso*quinoline*, which crystallises in slender needles, is volatile with steam, and melts at 95·5—96°.

4-Ethoxyphthalylglycine ethyl ester is converted by methyl-alcoholic sodium methoxide into *methyl* 4-*hydroxy*-6-(or 7)-*methoxy*iso*carbostyril*-3-*carboxylate*, $C_{12}H_{11}O_5N$, which crystallises from methyl alcohol in colourless needles and melts and decomposes at 248°.

On oxidation of an acid solution of 1 : 4 : 6- or 1 : 4 : 7-trihydroxy-*iso*quinoline with hydrogen peroxide, a *dihydroxycarbindigotin*, $OH\cdot C_6H_3{<}{\substack{CO\cdot NH\\CO}}{>}C{:}C{<}{\substack{NH\cdot CO\\CO}}{>}C_6H_3\cdot OH$, is obtained; it is also formed, but more slowly, by the atmospheric oxidation of an alkaline solution of the trihydroxy*iso*quinoline, and by crystallisation from concentrated sulphuric acid is obtained in red needles.

4-*Ethoxyphthalylalanine*, $OEt\cdot C_6H_3{:}(CO)_2{:}N\cdot CHMe\cdot CO_2H$, prepared by adding alanine to fused 4-ethoxyphthalic anhydride at 145—150°, crystallises from water in elongated leaflets and melts at 146°; the *ethyl* ester, $C_{15}H_{17}O_5N$, crystallises from alcohol, melts at 78°, and is transformed by alcoholic sodium ethoxide at 100° into 3-*methyl*-4-*hydroxy*-6-(or 7)-*ethoxy*iso*carbostyril*, which crystallises from water with $1H_2O$ and decomposes at 285°; on hydrolysis with concentrated hydriodic acid, the ethoxy-derivative gives 3-*methyl*-1 : 4 : 6- or 1 : 4 : 7-*trihydroxy*-iso*quinoline*, crystallising from water and decomposing at 240°.

W. A. D.

Ammonium Compounds. XVII. Formation of Non-oxygenated Tertiary Bases from Cyclammonium Hydroxides. HERMAN DECKER and THEODOR HOCK (*Ber.*, 1904, **37**, 1564—1569).—*9-Benzylacridine*, $C_6H_4<{C(C_7H_7) \atop N}>C_6H_4$, prepared by heating phenylacetic acid, diphenylamine, and zinc chloride for 20 hours at 180—200°, crystallises in bright yellow, volatile leaflets and melts at 173°; the *picrate*, $C_{26}H_{18}O_7N_4$, forms yellow crystals and melts at 230°. The *methiodide*, $C_6H_4<{C(C_7H_7) \atop NMeI}>C_6H_4$, prepared by the direct addition of methyl iodide at 100°, crystallises in small, dark red cubes; the analogous *9-benzylacridinium 10-methopicrate*, $C_{27}H_{20}O_7N_4$, prepared by precipitating the methiodide with alcoholic picric acid, melts at 189°. On decomposing the quaternary salts with sodium hydroxide, *9-benzylidene-10-methyl-9 : 10-dihydroacridine*, $C_6H_4<{C(:CHPh) \atop NMe}>C_6H_4$, is obtained, probably owing to the following series of changes occurring:

$$C_6H_4<{C(CH_2Ph) \atop NMe(OH)}>C_6H_4 \longrightarrow C_6H_4<{C(OH)(CH_2Ph) \atop NMe}>C_6H_4$$
$$\longrightarrow C_6H_4<{C(:CHPh) \atop NMe}>C_6H_4;$$

the product crystallises from benzene or light petroleum in large, bright yellow cubes, melts at 141°, and combines with picric acid to form the foregoing 9-benzylacridinium 10-methopicrate. It is slowly oxidised in the air giving benzaldehyde and 10-methyl-9-acridone, $C_6H_4<{CO \atop NMe}>C_6H_4$.

The foregoing changes are of importance, principally on account of the light that they throw on the nature of the *iso*papaverine bases (Decker and Clausen, this vol., i, 338). W. A. D.

Nitroso-*m*-phenylenediamine. K. BERTELS (*Ber.*, 1904, **37**, 2276—2282. Compare Täuber and Walder, Abstr., 1900, i, 566).—Nitroso-*m*-phenylenediamine is oxidised by hydrogen peroxide, in presence of ammonia, to nitrophenylenediamine $[NO_2:(NH_2)_2 = 1:2:4]$, which melts at 157° (Barbaglia, *Ber.*, 1874, **7**, 1257, gives m. p. 161°).

When warmed with aqueous sodium hydroxide, nitroso-*m*-phenylenediamine evolves ammonia and forms *4-nitroso-3-aminophenol*, which crystallises in long, red needles, melts and decomposes at about 200°, loses ammonia when acted on by concentrated aqueous alkali hydroxides, and is reduced by stannous chloride in hydrochloric acid solution to 3 : 4-diaminophenol. Contrary to Köhler's statement (Abstr., 1884, 1159), the hydrochloride of 3 : 4-diaminophenol is not soluble in concentrated hydrochloric acid.

m-Phenylenediamine condenses with benzaldehyde to form a *triphenylmethane* derivative, which gives a strong, yellow fluorescence when heated with hydrochloric acid at 160—170°. Nitroso-*m*-phenylenediamine, when warmed with benzaldehyde, forms a *dibenzylidene* derivative, which melts and decomposes at 240°. When

nitroso-*m*-phenylenediamine is heated with benzylidene chloride, or with benzaldehyde and hydrochloric acid, or when the dibenzylidene derivative is boiled with dilute hydrochloric acid, a *benziminazole* compound, $C_{13}H_{11}ON_3$, is formed. This crystallises in delicate, yellow needles, melts at 164°, and forms red dyes when diazotised and coupled with β-naphthol or naphthionic acid. With benzaldehyde, 4-nitroso-3-aminophenol condenses in a similar manner; the *product* contains H_2O. G. Y.

Dyes of the Diphenylnaphthylmethane, Phenyldinaphthylmethane, and Trinaphthylmethane Series. EMILIO NOELTING [and, in part, GEORG FREYSS, SERRA, DREYFUS, BOURRY, and JULES DEMANT] (*Ber.*, 1904, **37**, 1899—1920).—Derivatives of diphenylnaphthylmethane have been studied by Nathanson and Müller (Abstr., 1889, 1188), and derivatives of phenyldinaphthylmethane by Friedländer and Wellmanns (Abstr., 1889, 150); trinaphthylmethane compounds have not hitherto been described.

Diaminophenylnaphthyl ketones may be prepared by condensing dimethyl-*p*-aminobenzomethylanilide with alkylated α-naphthylamines by means of phosphorus oxychloride. The red aurammonium chlorides thus obtained are decomposed by alcohol and sodium hydroxide, yielding the ketones.

Dimethylaminophenyl methylaminonaphthyl ketone,

$$NHMe\cdot C_{10}H_6\cdot CO\cdot C_6H_4\cdot NMe_2,$$

forms bright yellow crystals and melts at 211—212°. *Dimethylaminophenyl ethylaminonaphthyl ketone*, $C_{21}H_{22}ON_2$, forms green, prismatic crystals and melts at 162°; *dimethylaminophenyl anilinonaphthyl ketone*, $C_{25}H_{22}ON_2$, forms bright yellow needles and melts at 201—202°; *dimethylaminophenyl methylanilinonaphthyl ketone*,

$$C_6H_4Me\cdot NH\cdot C_{10}H_6\cdot CO\cdot C_6H_4\cdot NMe_2,$$

forms bright yellow needles and melts at 221°; *diethylaminophenyl methylaminonaphthyl ketone*, $C_{22}H_{24}ON_2$, forms large, yellow crystals and melts at 149°; the *ethyl* compound forms green or yellow crystals and melts at 133·5°; *diethylaminophenyl anilinonaphthyl ketone*,

$$C_{27}H_{26}ON_2,$$

forms thick, yellow crystals and melts at 146—147°; *diethylaminophenyl methylanilinonaphthyl ketone*, $C_{28}H_{28}ON_2$, forms greenish-yellow needles and melts at 176—177°.

The ketones are weak bases, dissolving in concentrated acids, but being reprecipitated on dilution. Sodium amalgam reduces their alcoholic solutions, forming the corresponding hydrols. Fusion with zinc chloride and ammonium chloride converts them into auramines. The *auramine* $NHEt\cdot C_{10}H_6\cdot C(NH)\cdot C_6H_4\cdot NMe_2$ forms large, slightly yellow prisms and melts at 199—200°, its *hydrochloride* forms red prisms. The *auramine* $NHPh\cdot C_{10}H_6\cdot C(NH)\cdot C_6H_4\cdot NMe_2$ melts at 186° and the *auramine* $C_7H_7\cdot NH\cdot C_{10}H_6\cdot C(NH)\cdot C_6H_4\cdot NMe_2$ at 164—165°.

Tetramethyldiaminodiphenylaminonaphthylmethane,

$$NH_2\cdot C_{10}H_6\cdot CH(C_6H_4\cdot NMe_2)_2,$$

forms glistening leaflets and melts at 221—222°; its *acetyl* derivative forms colourless crystals and melts at 228—229°. The *methylamino-*

naphthyl compound melts at 201—202°, the corresponding *ethyl* derivative at 172—173°, the *phenyl* derivative at 167—168° (compare Nathanson and Müller, *loc. cit.*), and the p-*tolyl* derivative at 193—194°.

Tetramethyldiaminodiphenyl-diaminonaphthylmethane, from tetramethyldiaminobenzhydrol and *o*-naphthylenediamine, melts at 233—234°, and its *diacetyl* derivative at 258—259°. The *base*, $C_{41}H_{34}N_4$, obtained by condensing the diaminonaphthyl compound with phenanthraquinone, forms small, yellow needles and melts above 336°.

Dimethylaminophenyldimethyldiaminodinaphthylmethane,

$$NMe_2 \cdot C_6H_4 \cdot CH(C_{10}H_6 \cdot NHMe)_2,$$

forms a yellow, amorphous powder, without definite melting point; the *diethyl* derivative forms thick, colourless prisms and melts at 220°; the *diphenyl* and *di*-p-*tolyl* derivatives form white, amorphous powders without definite melting point.

Nitrodimethylaminophenyldimethyldiaminodinaphthylmethane, from 3-nitro-4-dimethylaminobenzaldehyde and methyl-α-naphthylamine, forms an amorphous powder, the *diethyl* derivative forms red prisms, and melts at 200°; the *diphenyl* and *di*-p-*tolyl* derivatives are yellow, amorphous powders without definite melting point.

Triethyltriaminotrinaphthylmethane, from ethyl orthoformate and ethyl-α-naphthylamine, forms colourless, glistening needles and melts above 300°.

The colouring matters obtained by the oxidation of these leucobases, or by direct condensation, are also described and tabulated. They form blue, or greenish-blue crystals with metallic lustre, the shade becoming greener as the number of naphthyl groups is increased. C. H. D.

Constitution of the Cyanine Dyes. A. Miethe and Gilbert Book (*Ber.*, 1904, 37, 2008—2022).—On adding potassium hydroxide to an alcoholic solution of quinoline ethiodide, a dye of the cyanine series is not obtained, showing that the presence of a methyl group, such as exists in quinaldine or lepidine, is necessary for the condensation; quinaldine ethiodide, on the other hand, is readily converted into a dye by alcoholic alkali. Ethyl-red (diethyl*iso*cyanine), which is obtained by the action of potassium hydroxide on a mixture of quinoline and quinaldine ethiodides in various proportions, best when the quinoline and quinaldine are in the molecular ratio 2 : 1, is considered to have the structure $\begin{matrix} CH{=}CH \\ | \\ NEt \cdot C_6H_4 \end{matrix}\!\!>\!C{:}CH \cdot C\!\!<\!\!\begin{matrix} CH_2{-}CH_2 \\ | \qquad | \\ NEtI \cdot C_6H_4 \end{matrix}$. The quinoline ethiodide is first probably converted into α-quinolone, thus:

$$C_6H_4\!<\!\begin{matrix} NEtI{:}CH \\ CH{=}CH \end{matrix} \longrightarrow C_6H_4\!<\!\begin{matrix} NEt(OH){:}CH \\ CH{=\!=}CH \end{matrix} \longrightarrow C_6H_4\!<\!\begin{matrix} NEt \cdot CH \\ CO{-}CH \end{matrix} + H_2;$$

the hydrogen formed reduces quinaldine ethiodide to a hydroquinaldine ethiodide, which then condenses with α-quinolone, giving the cyanine dye:

$$\begin{matrix} CH{=}CH \\ | \\ NEt \cdot C_6H_4 \end{matrix}\!\!>\!CO + CH_3 \cdot C\!\!<\!\!\begin{matrix} CH_2{-}CH_2 \\ | \qquad | \\ NEtI \cdot C_6H_4 \end{matrix} \longrightarrow \text{ethyl red} + H_2O.$$

The new formula explains the fact that the additive product formed

by ethyl-red with iodine is not a periodide, like quinoline periodide, but has properties agreeing more closely with the formula

$$\begin{matrix} CH{=}CH \\ | \qquad\quad \\ NEt\cdot C_6H_4 \end{matrix}\!\!>CI\cdot CHI\cdot C\!<\!\!\begin{matrix} CH_2{-}CH_2 \\ \quad | \\ NEtI\cdot C_6H_4 \end{matrix};$$

thus it does not impart a blue colour to starch paste even in presence of acid, and is decolorised by hydrochloric acid, whereas quinoline periodide at once turns starch blue and does not lose its colour in presence of dilute hydrochloric acid.

When 3 mols. of quinaldine ethiodide are heated with two mols. of alcoholic potassium hydroxide, a cyanine dye, $C_{24}H_{27}N_2I$, is produced, which is homologous with ethyl-red; it probably has the structure

$$\begin{matrix} CMe{=}CH \\ | \qquad\quad \\ NEt\cdot C_6H_4 \end{matrix}\!\!>C{:}CH\cdot C\!<\!\!\begin{matrix} CH_2{-}CH_2 \\ \quad | \\ NEtI\cdot C_6H_4 \end{matrix}.$$

It is much less valuable as a sensitiser of gelatin bromide plates than ethyl-red, as is shown by the curves of induced sensibility which are given for the two substances.

Silver nitrate converts ethyl-red into a *nitrate*, $C_{23}H_{25}N_2(NO_3)$, which crystallises in large, dark green prisms and is formed by a replacement of the iodine atom by the radicle NO_3. W. A. D.

Ethyl Benzoylpyruvate and its Derivatives. CARL BÜLOW (*Ber.*, 1904, 37, 2198—2209. Compare Abstr., 1903, i, 647).—Ethyl benzoylpyruvate reacts with methylamine to form dimethoxamide, $C_2O_2(NHMe)_2$, acetophenone, and alcohol.

Hydrazine and ethyl benzoylpyruvate in glacial acetic acid solution yield *ethyl 5-phenylpyrazole-3-carboxylate*, which crystallises from dilute alcohol in large needles, melts at 140°, and dissolves readily in organic solvents. Two mols. of hydrazine in alcoholic solution yield oxalodihydrazide, together with *hydrazine 5-phenylpyrazole-3-carboxylate*, $C_{10}H_{12}O_2N_4$, which crystallises from hot water in glistening, white leaflets, and melts at 203° and decomposes at 255°, the residue again solidifying to a white mass. When boiled with a small quantity of water, the salt dissolves, but rapidly deposits *5-phenylpyrazole-3-carboxylic hydrazide*, $C_3N_2H_2Ph\cdot CO\cdot NH\cdot NH_2$, melting at 205°.

5-Phenylpyrazole-3-carboxylic acid, prepared by hydrolysis of the ester, melts and decomposes at 231—232° (compare Wenglein, Diss. Jena, 1895).

Diazobenzene chloride and ethyl benzoylpyruvate form *ethyl benzeneazobenzoylpyruvate*, $COPh\cdot CH(N{:}NPh)\cdot CO\cdot CO_2Et$, crystallising from alcohol in yellow needles and melting at 115—116°. Phenylhydrazine acetate converts it into *ethyl 1 : 5-diphenyl-4-benzeneazopyrazole-3-carboxylate*, crystallising in orange leaflets and melting at 148—149°.

*Ethyl 5-phenyl-4-benzeneazo*iso*oxazole-3-carboxylate* from ethyl benzeneazobenzoylpyruvate and hydroxylamine forms yellow needles and melts at 99—100°. The corresponding *acid*, $C_{16}H_{11}O_3N_3$, is produced at the same time and melts at 217°. Alcoholic potassium hydroxide decomposes the *iso*oxazole ester, forming *benzeneazobenzoylacetonitrile*, $OH\cdot CPh{:}C(CN)\cdot N{:}NPh$, crystallising in yellow needles and melting at 135—136°.

Ethyl benzeneazobenzoylpyruvate and hydrazine hydrate form

5-*phenyl-4-benzeneazopyrazole-3-carboxylic acid*, separating from dilute acetic acid in reddish-brown crystals with golden lustre, and melting and decomposing at 247—248°, together with the *ethyl ester* melting at 153°.

Sodium benzoylpyruvate and diazobenzene chloride form *benzeneazo-benzoylpyruvic acid*, crystallising from dilute alcohol in slender, yellow needles and decomposing at 140—150°.

Ethyl o-*benzoic-acid-azobenzoylpyruvate*,

$$COPh\cdot CH(N\colon N\cdot C_6H_4\cdot CO_2H)\cdot CO\cdot CO_2Et,$$

from ethyl benzoylpyruvate and diazotised anthranilic acid, crystallises from dilute acetic acid in yellow needles and melts and decomposes at 158—160°. The *disazo*-compound from benzidine forms a brown, crystalline powder. C. H. D.

5-Chloro-1-*o*-tolyl-3-methylpyrazole and 1-Phenyl-3-methyl-5-pyrazolone-2′-carboxylic Acid. AUGUST MICHAELIS and C. EISENSCHMIDT (*Ber.*, 1904, 37, 2228—2231. Compare Abstr., 1900, i, 696). —When heated with phosphorus oxychloride for 10 hours at 150°, Knorr's *o*-tolylmethylpyrazolone yields 5-*chloro*-1-o-*tolyl*-3-*methyl pyrazole*, which crystallises from alcohol in colourless crystals melting at 56°. It turns red on exposure to the air, and is soluble in concentrated hydrochloric acid. The *methiodide*, $C_{12}H_{14}N_2ClI$, crystallises in colourless plates melting at 231—232°; the *methochloride* crystallises from water with $2H_2O$, which it loses at 112°, and then melts at 210°; its *picrate*, $C_{12}H_{14}N_2Cl\cdot O\cdot C_6H_2(NO_2)_3$, forms a yellow precipitate.

On oxidation, the *o*-tolylpyrazole derivative yields 5-*chloro*-1-*phenyl*-3-*methylpyrazole-2′-carboxylic acid*, $\begin{matrix}CMe{=}N\\ | \\ CH\colon CCl\end{matrix}\!\!>\!N\cdot C_6H_4\cdot CO_2H$, which crystallises from dilute acetic acid in colourless needles melting at 169° and is insoluble in water. The *barium* salt containing $3H_2O$, *calcium* salt which is anhydrous, and the *ethyl ester*, a colourless oil distilling at 315°, have been prepared.

When heated, the chloro-acid loses hydrogen chloride, yielding the *anhydride*, $CMe\!<\!\begin{matrix}N{-}N\cdot C_6H_4\\ \quad | \\ CH\colon C{-}{-}O\end{matrix}\!>\!CO$, which melts at 109° and boils at 345°. The anhydride combines with water forming 1-*phenyl*-3-*methylpyrazolone-2′-carboxylic acid* melting at 139°. J. J. S.

Pyrimidine Derivatives. 5-Methylcytosine. HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1904, 31, 591—606. Compare Abstr., 1903, i, 524, 526).—2-*Ethylthiol*-5-*methyl*-6-*oxypyrimidine*, $NH\!<\!\begin{matrix}C(SEt)\colon N\\ CO{-}CMe\end{matrix}\!>\!CH$, obtained by the action of ψ-ethylthiocarbamide hydrobromide on ethyl sodioformylpropionate, crystallises from hot water in long, slender prisms, melts at 158—159°, and is very soluble in alcohol. When this compound is warmed with phosphorus pentachloride, it is converted into 6-*chloro*-2-*ethylthiol*-5-*methylpyrimidine*, $N\!<\!\begin{matrix}C(SEt)\colon N\\ CCl{-}CMe\end{matrix}\!>\!CH$, which forms a colourless, oily

liquid and boils at 146—147° under 17 mm. and at 157—159° under 25—26 mm. pressure. 6-Chloro-2-ethylthiolpyrimidine boils at 135° under 24 mm. pressure. 6-*Amino*-2-*ethylthiol*-5-*methylpyrimidine*, $N{<}\begin{matrix}C(SEt)\text{=}N\\C(NH_2)\cdot CMe\end{matrix}{>}CH$, obtained by heating 6-chloro-2-ethylthiol-5-methylpyrimidine with alcoholic ammonia, crystallises in colourless prisms, melts at 96—97°, and is readily soluble in alcohol and sparingly so in water. By the action of alcoholic ammonia on 6-chloro-2-ethylthiolpyrimidine, 6-*ethoxy*-2-*ethylthiolpyrimidine*, $N{<}\begin{matrix}C(SEt)\text{=}N\\C(OEt)\cdot CH\end{matrix}{>}CH$, is produced, which boils at 137—138° under 18 mm. pressure, and, when heated with concentrated hydrochloric acid, is converted quantitatively into uracil.

When 6-amino-2-ethylthiolpyrimidine is heated with concentrated hydrochloric acid for 3—4 hours on the water-bath, 6-amino-2-oxypyrimidine (cytosine) *dihydrochloride* is obtained which crystallises in flat, colourless prisms. If 6-amino-2-ethylthiol-5-methylpyrimidine is treated in a similar manner, 6-amino-5-methyl-2-oxypyrimidine *hydrochloride* is produced, which melts and decomposes at 288°; a basic *hydrochloride* and a basic *hydrobromide* are also described. 6-*Amino*-5-*methyl*-2-*oxypyrimidine* (5-*methylcytosine*), $N{<}\begin{matrix}CO\text{——}NH\\C(NH_2)\cdot CMe\end{matrix}{>}CH$, forms colourless, prismatic crystals containing $\frac{1}{2}H_2O$, melts and decomposes at 270°, is soluble in water at 25° to the extent of 4·5 per cent., and yields a white precipitate with phosphotungstic acid; its *acetyl* derivative crystallises in needles and decomposes between 255° and 290°; the *picrate* and *platinichloride* are also described.

5-*Bromo*-2-*ethylthiol*-6-*oxypyrimidine*, $NH{<}\begin{matrix}C(SEt){:}N\\CO\text{—}CBr\end{matrix}{>}CH$, obtained by the action of bromine on 2-ethylthiol-6-oxypyrimidine, crystallises in colourless, acicular prisms, melts at 189°, is soluble in alcohol and sparingly so in water, and, when boiled with hydrochloric acid, is converted into 5-bromouracil. When 5-bromo-2-ethylthiol-6-oxypyrimidine is warmed with phosphorus pentachloride, 6-*chloro*-5-*bromo*-2-*ethylthiolpyrimidine*, $N{<}\begin{matrix}C(SEt){:}N\\CCl\text{—}CBr\end{matrix}{>}CH$, is produced, which forms colourless plates and melts at about 27°. 5-*Bromo*-6-*amino*-2-*ethylthiolpyrimidine*, $N{<}\begin{matrix}C(SEt)\text{=}N\\C(NH_2)\cdot CBr\end{matrix}{>}CH$, obtained by the action of alcoholic ammonia on 6-chloro-5-bromo-2-ethylthiolpyrimidine, crystallises in colourless prisms, melts at 123—124°, and dissolves readily in alcohol and sparingly in water. When this compound is boiled with strong hydrochloric acid, it is converted into 5-*bromo*-6-*amino*-2-*oxypyrimidine* (5-*bromocytosine*), $N{<}\begin{matrix}CO\text{——}NH\\C(NH_2)\cdot CBr\end{matrix}{>}CH$, which crystallises in acicular prisms and decomposes above 235°. 6-*Nitroamino*-2-*oxypyrimidine* (*nitrocytosine*), $N{<}\begin{matrix}CO\text{——}NH\\C(NH\cdot NO_2)\cdot CH\end{matrix}{>}CH$, prepared by the action of a mixture of nitric and sulphuric acids on anhydrous cytosine, crystallises in minute, colourless needles, darkens at 280°, and decomposes rapidly above 300°.

E. G.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. VI. Tolyl and Benzyl Derivatives of Furodiazole [1 : 2 : 4-Oxadiazole] and 1 : 3 : 4-Thiodiazole. ROBERT STOLLÉ and HENRY P. STEVENS (*J. pr. Chem.*, 1904, [ii], 69, 366—381. Compare Abstr., 1899, i, 456; 1903, i, 721; this vol., i, 102, 200, 453).—o-*Toluoylhydrazide*, formed by the action of boiling ethyl *o*-toluate on hydrazine hydrate, crystallises in delicate needles, melts at 124°, is easily soluble in alcohol, chloroform, acetone, or glacial acetic acid, and reduces ammoniacal silver solutions in the cold, but Fehling's solution only on warming. o-*Toluoylbenzylidenehydrazone*,

$$C_7H_7\cdot CO\cdot NH\cdot N:CHPh,$$

crystallises in white needles and melts at 164°. o-*Toluoylhydroxybenzylidenehydrazone* crystallises in yellow needles and melts at 166°.

s-*Di*-o-*toluoylhydrazide*, formed by the action of iodine on *o*-toluoylhydrazide in warm alcoholic solution, or along with di-*o*-tolyloxadiazole by the action of ethyl *o*-toluate on *o*-toluoylhydrazide in a sealed tube at 150°, crystallises in delicate, white needles, melts at 216—217°, and is soluble in dilute aqueous sodium hydroxide, alcohol, acetone, and chloroform.

2 : 5-*Di*-o-*tolyl*-1 : 3 : 4-*oxadiazole*, $\begin{matrix} N:C(C_7H_7) \\ | \\ N:C(C_7H_7) \end{matrix}\!\!>\!O$, is formed when *s*-di-*o*-toluoylhydrazide is heated at 300°. It distils under reduced pressure, crystallises in white needles, and melts at 121°. It is easily soluble in acetone, chloroform, or petroleum, but only moderately so in ether. It dissolves in concentrated sulphuric acid and is reprecipitated on addition of water. With silver nitrate in alcoholic solution, it forms an *additive* compound, $C_{16}H_{14}ON_2,2AgNO_3$, which crystallises from alcohol, melts at about 156°, and decomposes violently when heated above its melting point.

m-Toluoylhydrazide, prepared in the same way as the *ortho*-compound, crystallises in glistening leaflets and melts at 97°. m-*Toluoylbenzylidenehydrazone* crystallises in needles and melts at 139°. s-*Di*-m-*toluoylhydrazide* is formed by the same reactions as the *ortho*-compound, but no oxadiazole is obtained. It crystallises in clusters of needles and melts at 214—216°.

2 : 5-*Di*-m-*tolyl*-1 : 3 : 4-*oxadiazole* is obtained on heating *s*-di-*m*-tolylhydrazide at 300° and distilling the product under reduced pressure. The distillate is a colourless oil, which crystallises after a time and then melts at 72°. The *additive* compound with silver nitrate is a white, crystalline powder and melts at 206°.

p-*Toluoylhydrazide* crystallises in glistening leaflets and melts at 117°; p-*toluoylbenzylidenehydrazone* crystallises in small, white needles and melts at 235°; p-*toluoyl*-o-*hydroxybenzylidenehydrazone* crystallises in needles and melts at 197°. s-*Di*-p-*toluoylhydrazide* crystallises in delicate, white needles and melts at 250°. Of the hydrazides, the ortho-compounds are the most easily, the para- the least easily soluble.

2 : 5-Di-*p*-tolyl-1 : 3 : 4-oxadiazole, formed when *s*-di-*p*-tolylhydrazide is heated at 300°, crystallises from alcohol in large, colourless needles and melts at 175°. Pinner (Abstr., 1895, i, 138) gives the melting point as 233—234°. The silver nitrate additive compound,

$$C_{16}H_{14}ON_2,AgNO_3,$$

is a crystalline powder which melts at 235°. Pinner (*loc. cit.*) found it to decompose above 280°.

When heated at 300°, *s*-diphenylacetylhydrazide (Boetzelen, Abstr., 1902, i, 58) yields phenylacetonitrile, which boils at 230—240°, and, with benzaldehyde and alcoholic potassium hydroxide, forms α-phenylcinnamonitrile. 2 : 5-*Dibenzyl*-1 : 3 : 4-*oxadiazole* is formed when *s*-diphenylacetylhydrazide is heated at 260—280°, or in better yield when the hydrazide is heated with zinc chloride. It crystallises in yellow needles and melts at 98°. With silver nitrate, it forms a crystalline *additive* compound which melts at about 120°.

These 1 : 3 : 4-oxadiazoles are stable compounds which can be boiled with alkalis or dilute acids without undergoing any change.

2 : 5-*Di*-p-*tolyl*-1 : 3 : 4-*thiodiazole*, $\begin{matrix} N\colon C(C_7H_7) \\ | \\ N\colon C(C_7H_7) \end{matrix}\!\!>\!S$, is formed when *s*-di-*p*-toluoylhydrazide is heated with phosphorus pentasulphide at 300°. It crystallises in golden plates or short needles, melts at 156—158°, is easily soluble in alcohol, acetone, or chloroform, is precipitated from its solution in concentrated sulphuric acid on addition of water, and resembles the corresponding oxadiazole in its stability.

2 : 5-*Dibenzyl*-1 : 3 : 4-*thiodiazole*, prepared by the action of phosphorus pentasulphide on *s*-diphenylacetylhydrazide, crystallises in short, yellow needles and melts at 98°. It is easily soluble in ether, alcohol, acetone, or chloroform, is precipitated on addition of water to its solution in concentrated sulphuric acid, and remains unchanged when boiled with dilute acids or alkalis or when heated with dilute sulphuric acid in a sealed tube at 175°. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. VII. Conversion of *s*-Di-*m*-chlorobenzoylhydrazide into Diazole Derivatives. ROBERT STOLLÉ and HANS FOERSTER (*J. pr. Chem.*, 1904, [ii], 69, 382—384. Compare Abstr., 1902, i, 58).—2 : 5-*Di*-m-*chlorophenyl*-1 : 3 : 4-*oxadiazole*, $\begin{matrix} N\colon C(C_6H_4Cl) \\ | \\ N\colon C(C_6H_4Cl) \end{matrix}\!\!>\!O$, is formed when *s*-di-*m*-chlorobenzoylhydrazide is heated with phosphorus pentoxide at 300°. It crystallises in white needles, melts at 144°, and is easily soluble in ether, chloroform, or boiling alcohol. With silver nitrate in alcoholic solution, it forms an *additive* compound, $C_{14}H_8ON_2Cl_2,AgNO_3$, which crystallises in small, slender needles, melts at 210°, and is moderately sensitive to light.

2 : 5-*Di*-m-*chlorophenyl*-1 : 3 : 4-*thiodiazole*, obtained by heating a mixture of *s*-di-*m*-chlorobenzoylhydrazide and phosphorus pentasulphide at 250—300°, crystallises in short, white needles, melts at 151°, and is easily soluble in acetone, chloroform, or concentrated sulphuric acid. From its solution in sulphuric acid, it is precipitated unchanged on addition of water. It is not acted on by boiling dilute acids or alkalis.

2 : 5-*Di*-m-*chlorophenyltriazole*, $\begin{matrix} N\colon C(C_6H_4Cl) \\ | \\ N\colon C(C_6H_4Cl) \end{matrix}\!\!>\!NH$, prepared by heating *s*-di-*m*-chlorobenzoylhydrazide with zinc ammonio-chloride at 300°, crystallises from benzene and melts at 220°. G. Y.

Isomerism in the Amidine Series: Diphenylbenzenylamino-amidine and Phenylbenzenylphenylaminoamidine. Henry L. Wheeler and Treat B. Johnson (*Amer. Chem. J.*, 1904, 31, 577—584. Compare Abstr., 1903, i, 693).—The statements of Acree (Abstr., 1902, i, 242; 1903, i, 867) with regard to the possibility of desmotropism in the amidine series are discussed, and it is maintained that no evidence of such isomerism in this class of compounds has yet been discovered.

When diphenylbenzenylaminoamidine, the more fusible amidine described by Pechmann (Abstr., 1896, i, 31), is treated with nitrous acid, diphenylbenzenylamidine is produced. The *benzoyl* derivative of diphenylbenzenylaminoamidine crystallises in colourless, rhombic plates and melts at 136°. When the less fusible amidine is treated with benzoic anhydride, no benzoyl derivative is obtained.

By the action of carbonyl chloride on phenylbenzenylphenylamino-amidine (Pechmann's less fusible amidine), 1 : 3 : 4-triphenyl-1 : 2 : 4-triazolone is obtained, melting at 217—218°. The more fusible amidine combines readily with phenylthiocarbimide with formation of a cream-coloured powder which does not melt below 345° and is sparingly soluble in benzene or alcohol. The less fusible amidine also unites with phenylthiocarbimide with production of a *compound* which crystallises in needles, melts at about 186°, and is slightly soluble in alcohol. E. G.

Action of Cyanogen Bromide on Hydroxylamine. Heinrich Wieland (*Ber.*, 1904, 37, 1536—1542).—All attempts to prepare cyanohydroxylamine by the interaction of cyanogen bromide and hydroxylamine were fruitless; even at $-15°$ the action between the two substances could not easily be regulated. Cyanogen bromide, however, in ethereal solution converts phenylhydroxylamine into the *hydrobromide* of *diphenyldihydroxyguanidine*, $NH\!:\!C(NPh\cdot OH)_2$; the *base* forms colourless, felted needles, and cannot be recrystallised without decomposing. It melts and decomposes at 135°, and is easily reduced by stannous chloride and hydrochloric acid to diphenylguanidine.

Cyanophenylhydroxylamine, $OH\cdot NPh\cdot CN$, is obtained when cyanogen bromide and sodium hydrogen carbonate are added alternately to an alcoholic solution of phenylhydroxylamine cooled with ice; it crystallises from light petroleum (b. p. 50°) in dazzling, white spangles, melts and decomposes at 60°, and soon decomposes on keeping. The *dihydrochloride*, $C_7H_8N_2OCl_2$, which melts at 158°, is more stable. W. A. D.

Addition of Alkylcarbimides and Thiocarbimides to Primary Hydrazines. Max Busch, Erich Opfermann, and H. Walther (*Ber.*, 1904, 37, 2318—2333).—Busch and Holzmann (Abstr., 1901, i, 234) have shown that the isomerism discovered by Marckwald (Abstr., 1893, i, 46) with thiosemicarbazides is due to the transference of the thiocarbimide grouping from the α- to the β-nitrogen atom of the hydrazine during the conversion of the labile into the stable thiosemi-

carbazide. The addition of thiocarbimides to primary alphyl hydrazines has now been examined, and it is found that methyl- and benzylhydrazines add on thiocarbimides at the α-nitrogen atom; the addition at this particular point in the molecule is not conditioned by temperature, and the $\beta\delta$-compounds obtained do not, as a rule, suffer transformation into the $\alpha\delta$-isomerides. The same regularity obtains when alkylcarbimides are substituted for thiocarbimides.

The compound described by Marckwald and Sedlaczek as dimethylthiosemicarbazide was prepared by the methods used by these authors and shown to be $\beta\delta$-dimethylthiosemicarbazide, $NHMe\cdot CS\cdot NMe\cdot NH_2$. m-*Nitrobenzaldehydedimethylthiosemicarbazone*,

$$NHMe\cdot CS\cdot NMe\cdot N:CH\cdot C_6H_4\cdot NO_2,$$

crystallises in glistening, yellow needles and melts at 227—228°. Methylhydrazine and allylthiocarbimide unite to form *β-methyl-δ-allylthiosemicarbazide*, $C_3H_5\cdot NH\cdot CS\cdot NMe\cdot NH_2$, which crystallises in transparent plates and melts at 57°; it does not suffer rearrangement into the isomeric $\alpha\delta$-compound; it condenses with *m*-nitrobenzaldehyde to form m-*nitrobenzaldehydemethylallylthiosemicarbazone*, which crystallises from alcohol in yellow needles and melts at 132°. β-Methyl-δ-phenylthiosemicarbazide, $NHPh\cdot CS\cdot NMe\cdot NH_2$, had previously been prepared by Marckwald and Sedlaczek, and had been classified by them as a labile (anti-) thiosemicarbazide; it readily condenses with benzaldehyde to form *benzaldehydephenylmethylthiosemicarbazone*,

$$NHPh\cdot CS\cdot NMe\cdot N:CHPh,$$

which melts at 132°. *Phenylmethylthiosemicarbazide methyl ether* is a yellow oil, which combines with benzenesulphonic chloride to form the *sulphone*, which crystallises in white needles melting at 93—94°. Further proof of the constitution of the methyl ether is afforded by its behaviour towards carbon disulphide, with which it forms dithiocarbazinic acid, $SMe\cdot NPh\cdot NMe\cdot NH\cdot CS\cdot SH$. The methyl ether readily condenses with benzaldehyde to form *benzaldehydephenylmethylsemicarbazide*, $NHPh\cdot CO\cdot NMe\cdot N:CHPh$, which forms white needles melting at 108°; methyl mercaptan is also produced in the reaction.

β-Methyl-δ-ethylsemicarbazide, $NHEt\cdot CO\cdot NMe\cdot NH_2$, prepared from methylhydrazine and ethylcarbimide, separates from alcohol in needles, melts at 154—155°, and reduces Fehling's solution. m-*Nitrobenzaldehydemethylethylsemicarbazone* forms yellow needles and melts at 142—143°.

δ-Phenyl-β-methylsemicarbazide, $NHPh\cdot CO\cdot NMe\cdot NH_2$, formed from methylhydrazine and phenylcarbimide, melts at 93—94°. *Benzaldehydephenylmethylsemicarbazone* separates from alcohol in slender needles and melts at 108°.

Benzaldehydebenzylsemicarbazone melts at 153—154°.

β-Benzyl-δ-ethylsemicarbazide, $CH_2Ph\cdot N(CO\cdot NHEt)\cdot NH_2$, prepared from benzylhydrazine and ethylcarbimide, condenses with *m*-nitrobenzaldehyde to form m-*nitrobenzaldehydebenzylethylsemicarbazone*, which crystallises in yellow plates, melting at 106°.

δ-Phenyl-β-benzylsemicarbazide, $CH_2Ph\cdot N(CO\cdot NHPh)\cdot NH_2$, prepared from benzylhydrazine and phenylcarbimide, separates from alcohol in glassy crystals and melts at 109—110°; when warmed, it reduces Fehling's solution. *Benzaldehydephenylbenzylsemicarbazone* melts at 152°.

β-Benzyl-δ-methylthiosemicarbazide, $CH_2Ph\cdot N(CS\cdot NHMe)\cdot NH_2$, prepared from benzylhydrazine and methylthiocarbimide, separates from benzene in rhombohedra and melts at 129°. *Benzaldehydebenzylmethylthiosemicarbazone* melts at 147°.

β-Benzyl-δ-allylthiosemicarbazide, $CH_2Ph\cdot N(CS\cdot NH\cdot C_3H_5)\cdot NH_2$, separates from light petroleum in glassy prisms and melts at 61°. *Benzaldehydebenzylallylthiosemicarbazone* melts at 106—107°.

δ-Phenyl-β-benzylthiosemicarbazide, $CH_2Ph\cdot N(CS\cdot NHPh)\cdot NH_2$, prepared from benzylhydrazine and phenylthiocarbimide, separates from alcohol in glistening leaflets and melts at 123°. *Benzaldehydephenylbenzylthiosemicarbazone* melts at 132°. *Phenylbenzylthiosemicarbazide methyl ether* is a yellow oil, which, with benzenesulphonic chloride, forms the *sulphone,* separating from alcohol in prisms and melting at 126°. The methyl ether condenses with benzaldehyde to form the *benzylidene* derivative, $CH_2Ph\cdot N(C{:}NPh\cdot SMe)\cdot N{:}CHPh$, which crystallises in yellow needles and melts at 104°.

δ-Phenyl-β-benzylthiosemicarbazide is exceptional in undergoing transformation into *δ-phenyl-α-benzylthiosemicarbazide* at 130°; the latter compound melts at 155°.

α-Benzoyl-δ-phenylsemicarbazide, $NHBz\cdot NH\cdot CO\cdot NHPh$, prepared from benzoylhydrazide and phenylcarbimide, separates from alcohol in glistening leaflets and melts at 210°. It does not form a condensation product with benzaldehyde, nor does it reduce Fehling's solution.

β-Phenyl-δ-methylsemicarbazide hydrochloride melts at 177°. *Benzaldehydephenylmethylsemicarbazone* melts at 151—152°. *Phenylmethylsemicarbazide methyl ether* is a red oil, the main product of the condensation of which with benzaldehyde was the *benzylidene* derivative, $SMe\cdot C(NMe)\cdot NPh\cdot N{:}CHPh$, which melts at 136—137°.

α-Phenyl-δ-methylthiosemicarbazide, prepared according to Marckwald's directions, condenses with benzaldehyde to form endo*thiodiphenylmethyltriazole,* $MeN\begin{cases} CPh\text{—}NPh \\ >S \quad | \\ C\text{===}N \end{cases}$, which separates from a mixture of chloroform and alcohol in glistening, amber-coloured plates and melts at 242—243°. A. McK.

Transformations in the Urazole Series. II. Max Busch and Erich Opfermann (*Ber.*, 1904, 37, 2333—2338. Compare Abstr., 1902, i, 322 and preceding abstract).—The tautomeric phenomena observed by Marckwald and Sedlaczek with the product obtained by the action of carbonyl chloride on phenylmethylthiosemicarbazide have been studied by the authors with the triazole derivatives. Desmotropism was noted only in the cases of those triazoles which are derived from alphylhydrazines, whilst with derivatives of arylhydrazines, studied by Marckwald and his pupils and termed by them iminodiazolones, tautomerism was exhibited where the two isomerides could not be isolated.

5-*Thiol*-1-*benzyl*-4-*methyl*endo*xytriazole,* $NMe\begin{cases} C(SH)\cdot N\cdot CH_2Ph \\ >O \quad | \\ C\text{===}N \end{cases}$, prepared from carbonyl chloride and β-benzyl-δ-methylthiosemi-

carbazide, forms tiny needles and melts at 117°. At the temperature of its melting point, or by crystallising it from hot water, or by acidifying its hot alkaline solution, it is transformed into the more stable isomeride, 1-*benzyl*-4-*methylthiourazole*,

$$NMe<\begin{matrix}CS\cdot N\cdot CH_2Ph\\ CO\cdot NH\end{matrix},$$

which separates from water in silky needles and melts at 157°.

*Thiolbenzylallyl*endo*oxytriazole*, $C_3H_5\cdot N<\begin{matrix}C(SH)\cdot N\cdot CH_2Ph\\ >O \quad |\\ C{=\!=}N\end{matrix}$, prepared from carbonyl chloride and β-benzyl-δ-allylthiosemicarbazide, crystallises in needles, melts at 108°, and readily undergoes transformation into the more stable isomeride, *benzylallylthiourazole*,

$$C_3H_5\cdot N<\begin{matrix}CS\cdot N\cdot CH_2Ph\\ CO\cdot NH\end{matrix},$$

which crystallises in glistening needles and melts at 161°.

*Thiolphenylbenzyl*endo*oxytriazole*, $NPh<\begin{matrix}C(SH)\cdot N\cdot CH_2Ph\\ >O \quad |\\ C{=\!=}N\end{matrix}$, prepared from δ-phenyl-β-benzylthiosemicarbazide and carbonyl chloride, forms slender needles and melts at 147°. At its melting point, or when crystallised from alcohol, it undergoes rearrangement into *phenylbenzylthiourazole*, $NPh<\begin{matrix}CS\cdot N\cdot CH_2Ph\\ CO\cdot NH\end{matrix}$, which forms slender, silky needles and melts at 218°.

β-Phenyl-δ-methylthiosemicarbazide-α-carboxylic acid,

$$NHMe\cdot CS\cdot NPh\cdot NH\cdot CO_2H,$$

prepared from carbonyl chloride and β-phenyl-δ-methylthiosemicarbazide (compare Illgen, *Inaug. Diss. Berlin*, 1894), is readily transformed by heat into its inner anhydride, phenylmethylthiourazole, $NMe<\begin{matrix}CS\cdot NPh\\ CO\cdot NH\end{matrix}$, which melts at 203°. When phenylmethylthiourazole is heated with methyl iodide at 100°, methyl mercaptan is evolved and 1-phenyl-4-methylurazole is obtained, identical with the product previously described by Busch and Heinrichs (Abstr., 1901, i, 617). During the methylation, the thiourazole reacts as the tautomeric *endo*oxytriazolethiol. A. McK.

3 : 8-Diaminodiphenyleneazone. By Fritz Fichter and Paul Dieterle (*Zeit. Farb. Text. Chem.*, 1904, 37, 157).—3 : 8-Diaminodiphenyleneazone (Ullmann and Dieterle, this vol., i, 269) condenses with benzaldehyde in alcoholic solution to form the *dibenzylidene* derivative, $C_{26}H_{18}N_4$, which crystallises from xylene in lustrous, sulphur-yellow leaflets and melts at 210°; the analogous *difurfurylidene* derivative forms yellowish-brown leaflets and melts at 207°.

3 : 8-Diphenyleneazone, when diazotised in the usual way, condenses with sodium naphthionate forming a crimson dye which is directly applicable to cotton. The introduction of an azone ring into the benzidine nucleus in the ortho-position relatively to the diphenyl-

linking does not therefore destroy the direct dyeing properties of the base. W. A. D.

Synthesis of Xanthine Bases from Cyanoacetic Acid. Synthesis of Hypoxanthine and Adenine. WILHELM TRAUBE (*Annalen*, 1904, 331, 64—88. Compare Abstr., 1900, i, 416; 1901, i, 54).—In continuation of previous work on the synthesis of xanthine bases from cyanoacetic acid, the synthesis of hypoxanthine and adenine has now been achieved by condensing thiocarbamide (not guanidine, as in the earlier experiments) with ethyl cyanoacetate and malononitrile respectively.

4-*Amino-6-hydroxy-2-thiopyrimidine* (4-*amino-2-thiouracil*),

$$N{<}{\genfrac{}{}{0pt}{}{C(OH){\cdot}CH}{C(SH)=N}}{>}C{\cdot}NH_2 \quad\text{or}\quad NH{<}{\genfrac{}{}{0pt}{}{CO{\cdot}CH_2}{CS-NH}}{>}C{:}NH,H_2O,$$

is prepared by heating at 100° a solution of sodium ethoxide in absolute alcohol with a powdered mixture of mol. proportions of thiocarbamide and ethyl cyanoacetate, when the sodium salt of the pyrimidine separates; the pyrimidine crystallises in long needles from water, and forms crystalline salts with both acids and bases. The iso*nitroso*-derivative is prepared by adding sodium nitrite and acetic acid successively to a solution of the pyrimidine in alkali hydroxide, and is purified by conversion into the ammonium salt; the salts form well-developed crystals, which are fairly soluble in water.

4 : 5-*Diamino-6-hydroxy-2-thiopyrimidine* (4 : 5-*diamino-2-thiouracil*, $NH{<}{\genfrac{}{}{0pt}{}{CO{\cdot}C(NH_2)}{CS\text{———}NH}}{>}C{\cdot}NH_2$), is prepared by adding the *iso*nitrosopyrimidine to boiling 5 per cent. ammonium sulphide and precipitating the base from the ammoniacal liquor as formate. The base is obtained as yellowish-brown prisms by evaporating the ammoniacal solution. It forms a series of sparingly soluble salts with acids, and is readily soluble in alkali hydroxides. The ammoniacal solution reduces silver nitrate and gives a precipitate of lead sulphide. The *monoformyl* derivative, $C_5H_6O_2N_4S,H_2O$, prepared by heating the formate with formic acid, crystallises in colourless prisms, readily soluble in ammonia, and does not reduce silver solutions.

Thiohypoxanthine (6-*oxy-2-thiopurine*), $\genfrac{}{}{0pt}{}{NH{\cdot}CO{\cdot}C{\cdot}NH}{CS{\cdot}NH{\cdot}C\text{—}N}{>}CH$, is prepared by heating the solid sodium salt (prepared by precipitating an aqueous solution with alcohol) at 250—255°, dissolving the resulting sodium salt of the thiohypoxanthine in water, and precipitating with acetic acid; it crystallises in small needles. It is converted by heating with 25 per cent. nitric acid at 100° into hypoxanthine, which was shown to be completely identical with the natural product by conversion into the dimethyl derivative.

4 : 6-*Diamino-2-thiopyrimidine*, $SH{\cdot}C{<}{\genfrac{}{}{0pt}{}{N{:}C(NH_2)}{N{\cdot}C(NH_2)}}{>}CH,\frac{1}{2}H_2O$, is prepared by heating a mixture of malononitrile, thiocarbamide, and sodium ethoxide dissolved in alcohol, when the sodium salt crystallises out; from the aqueous solution of the latter, the pyrimidine is obtained by acidifying with acetic acid, and crystallises in prisms which do not

melt at 280°; it forms a crystalline *hydrochloride* and *sulphate* and an amorphous *platinichloride*, and dissolves readily in alkali hydroxides. The iso*nitroso*-derivative is obtained as a green solid by adding successively sodium nitrite and acetic acid to an alkaline solution of the pyrimidine.

4 : 5 : 6-*Triamino-2-thiopyrimidine*,

$$SH\cdot C<\begin{matrix} N:C(NH_2) \\ N\cdot C(NH_2) \end{matrix}>C\cdot NH_2, \tfrac{1}{2}H_2O,$$

is prepared by reducing the *iso*nitroso-derivative, just described, with 10 per cent. ammonium sulphide, and forms (from water) large, yellow, prismatic crystals; it forms a sparsely soluble *sulphate*, *nitrate*, and *hydrochloride*, and is also soluble in alkali hydroxides, but not in ammonia; it reduces ammoniacal silver nitrate very readily. The *monoformyl* derivative crystallises, with H_2O, in long, silky needles which soften at 140°, and is soluble both in acids and alkali hydroxides, acting towards the latter as a monobasic acid. The potassium salt, with H_2O, forms large, colourless crystals.

Thioadenine (6-*amino-2-thiopurine*), $\begin{matrix} N:C(NH_2)\cdot C\cdot NH \\ | \qquad\qquad\quad || \\ C(SH):N—C—N \end{matrix}>CH,H_2O$, is prepared by heating the potassium salt of the formyl derivative, just mentioned, at 230° for 40 minutes, when the potassium salt of the purine is formed; it forms pale yellow, insoluble crystals, and has both acid and basic properties, being readily soluble in alkali hydroxides, and forming crystalline salts with acids, of which the *sulphate* is easily prepared. After several trials, it was found that the thio-compound could only be converted into adenine by oxidation with hydrogen peroxide in the presence of acids. The synthetical adenine was proved to be identical with the natural product by identity of water of crystallisation, and of the behaviour of the sulphate towards reducing agents.
K. J. P. O.

2-Phenylhypoxanthine and 2-Phenyladenine. WILHELM TRAUBE and LUDWIG HERRMANN (*Ber.*, 1904, **37**, 2267—2272. Compare Abstr., 1900, i, 416).—4-*Amino-6-hydroxy-2-phenylpyrimidine*,

$$N<\begin{matrix} C(OH)\cdot CH \\ CPh=\!=\!=N \end{matrix}>C\cdot NH_2,$$

is formed by the action of sodium ethoxide and ethyl cyanoacetate on benzamidine. It crystallises in slender needles, melts at 252°, is soluble in dilute alkali hydroxides and acids, and forms a *sodium* compound and a *platinichloride*, which crystallises in long, yellow needles. The iso*nitroso*-compound, obtained by acting on 4-amino-6-hydroxy-2-phenylpyrimidine, crystallises in green needles and is soluble in dilute alkali hydroxides and ammonia to solutions which slowly deposit bluish-violet, crystalline *salts*. It is soluble with decomposition in mineral acids.

Reduction of the *iso*nitroso-compound with ammonium sulphide leads to the formation of 4 : 5-*diamino-6-hydroxy-2-phenylpyrimidine*, $N<\begin{matrix} C(OH)\cdot C(NH_2) \\ CPh=\!=\!=\!=N \end{matrix}>C\cdot NH_2$, which separates from alcohol in dark green crystals and forms a *hydrochloride*, $C_{10}H_{10}ON_4,HCl$. When

heated with formic acid, it yields 2-*phenylhypoxanthine*,

$$\begin{array}{l}\mathrm{N{:}C(OH){\cdot}C{\cdot}NH} \\ \mathrm{CPh{=}N{\cdot}C{-\!\!-}N}\end{array}\!\!>\mathrm{CH},$$

which is soluble in hot alcohol, yields a *hydrochloride* which is partly decomposed by water, forms an amorphous precipitate with silver nitrate in ammoniacal solution, and gives the murexide reaction. When heated with phosphorus oxychloride in a sealed tube at 140°, 2-phenylhypoxanthine yields 6-*chloro*-2-*phenylpurine*, which crystallises from alcohol in colourless, rhombic plates, and, with aqueous ammonia at 140° under pressure, forms 2-*phenyladenine*,

$$\begin{array}{l}\mathrm{N{:}C(NH_2){\cdot}C{\cdot}NH} \\ \mathrm{CPh{=}N{\cdot}C{-\!\!-}N}\end{array}\!\!>\mathrm{CH}.$$

This crystallises from hot water in slender, colourless needles, forms a neutral aqueous solution, and is precipitated from its ammoniacal or nitric acid solutions by silver nitrate. G. Y.

Constitution of Purpuric Acid and of Murexide. MAX SLIMMER and JULIUS STIEGLITZ (*Amer. Chem. J.*, 1904, 31, 661—679).—The generally accepted formula for purpuric acid is that proposed by Beilstein, namely, $\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CO}\\\mathrm{NH{\cdot}CO}\end{matrix}>\mathrm{C}\overset{\mathrm{NH}}{\diagup\!\!-\!\!-\!\!\diagdown}\mathrm{C}<\begin{matrix}\mathrm{CO{\cdot}NH}\\\mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO}$. The present paper shows that this conception is inaccurate, and that the constitution of the acid is best expressed by the formula

$$\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CO}\\\mathrm{NH{\cdot}CO}\end{matrix}>\mathrm{CH{\cdot}N{:}C}<\begin{matrix}\mathrm{CO{\cdot}NH}\\\mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO},$$

whilst in the hydrated salts it assumes the form

$$\mathrm{CO}<\begin{matrix}\mathrm{NH{\cdot}CO}\\\mathrm{NH{\cdot}CO}\end{matrix}>\mathrm{CH{\cdot}NH{\cdot}C(OH)}<\begin{matrix}\mathrm{CO{\cdot}NH}\\\mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO}.$$

When 1 : 3-dimethyluramil is treated with alloxan in presence of ammonium carbonate, *ammonium* 1 : 3-*dimethylpurpurate*,

$$\mathrm{CO}<\begin{matrix}\mathrm{NMe{-\!\!-\!\!-\!\!-}CO}\\\mathrm{NMe{\cdot}C(O{\cdot}NH_4)}\end{matrix}\!\!>\mathrm{C{\cdot}N{:}C}<\begin{matrix}\mathrm{CO{\cdot}NH}\\\mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO},$$

is produced, which crystallises in small, four-sided prisms and resembles ordinary murexide, but is slightly yellower in colour; when warmed with dilute hydrochloric acid, it is converted into dimethyluramil and alloxantin. By the condensation of uramil with dimethylalloxan, *ammonium* 1′ : 3′-*dimethylpurpurate*,

$$\mathrm{CO}<\begin{matrix}\mathrm{NH{-\!\!-\!\!-\!\!-}CO}\\\mathrm{NH{\cdot}C(O{\cdot}NH_4)}\end{matrix}\!\!>\mathrm{C{\cdot}N{:}C}<\begin{matrix}\mathrm{CO{\cdot}NMe}\\\mathrm{CO{\cdot}NMe}\end{matrix}>\mathrm{CO},$$

is obtained, which closely resembles its isomeride, but is decomposed by dilute hydrochloric acid with formation of dialuric acid amide and tetramethylalloxantin. These results show that the purpuric acid molecule is not symmetrical, and its constitution therefore cannot be correctly represented by Beilstein's formula.

By the condensation of 5-amino-4-methyluracil with alloxan, 4-*methyluraciliminoalloxan*,

$$\mathrm{CO}<\begin{matrix}\mathrm{NH{-\!\!-}CO}\\\mathrm{NH{\cdot}CMe}\end{matrix}\!\!>\mathrm{C{\cdot}N{:}C}<\begin{matrix}\mathrm{CO{\cdot}NH}\\\mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CO},$$

is obtained as a heavy, dark red precipitate. It follows, therefore, that the presence of the hydrogen attached to the carbon atom in the

uramil group is not essential to the formation of condensation products of the nature of purpuric acid, whereas, according to Beilstein's formula, such is the case.

The so-called water of crystallisation present in ammonium purpurate hydrate (murexide) and the corresponding potassium salt is constitutional; this is shown by the fact that salts of intensely coloured purpuric acid derivatives can be prepared from 7-alkyluramils and alloxan, which cannot lose the molecule of water, but in other respects resemble the purpurates. *Ammonium 7-methylpurpurate hydrate*,

$$CO<\begin{matrix}NH\text{———————}CO\\NH\cdot C(O\cdot NH_4)\end{matrix}>C\cdot NMe\cdot C(OH)<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

obtained by the condensation of 7-methyluramil and alloxan, crystallises in small, four-sided prisms and closely resembles ordinary murexide; this compound can also be prepared by the oxidation of 7-methyluramil with mercuric oxide, and by the action of methylamine on alloxantin. *Ammonium 7-ethylpurpurate hydrate* has similar properties.

When anhydrous potassium purpurate is heated with methyl iodide for 5 hours at 100° in a sealed tube, *5-methylpurpuric acid*,

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CMe\cdot N{:}C<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

is produced. By the action of methyl iodide on silver purpurate, *O-4-methyl purpurate*, $CO<\begin{matrix}NH\text{————}CO\\NH\cdot C(OMe)\end{matrix}>C\cdot N{:}C<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO$, is formed, which has a deep red colour and is very unstable. E. G.

Action of Benzene on Azoxybenzene in presence of Aluminium Chloride. ERNEST BANDROWSKI and ALEXANDER PROKOPECZKO (*Bull. Acad. Sci. Cracow*, 1904, 158—162).—Azoxybenzene reacts readily with benzene in presence of aluminium chloride. The chief products are benzeneazodiphenyl and azodiphenyl. Benzenehydrazodiphenyl may be obtained by reducing benzeneazodiphenyl; it melts at 122° and yields two isomeric diacetyl derivatives, one of which crystallises in leaflets, melts at 217°, and is sparingly soluble in alcohol, whilst the other readily dissolves in that medium and forms needles which melt at 176°.

Toluene and azoxybenzene give a *benzeneazomethyldiphenyl*,

$$N_2Ph\cdot C_6H_4\cdot C_6H_4Me,$$

which melts at 137° together with azoditolyl, $N_2(C_6H_4\cdot C_6H_4Me)_2$, which melts at 260°. *Benzenehydrazomethyldiphenyl*, $N_2H_2Ph\cdot C_6H_4\cdot C_6H_4Me$, melts at 102°. S. S.

Derivatives of 4′-Iodo-2 : 3′-dimethylazobenzene and of *m*-Bromoiodobenzene with Polyvalent Iodine. CONRAD WILLGERODT and PAUL LEWINO (*J. pr. Chem.*, 1904, [ii], 69, 321—333. Compare this vol., i, 485).—*4′-Iodo-2 : 3′-dimethylazobenzene*,

$$C_6H_4Me\cdot N_2\cdot C_6H_3MeI,$$

obtained by the action of potassium iodide on diazotised-4′-amino-2 : 3′-dimethylazobenzene, crystallises in golden needles, melts at 64°, has no odour, and is easily soluble in organic solvents, but is insoluble in water. The *iodochloride*, $C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot ICl_2$, prepared by chlor-

inating iododimethylazobenzene in chloroform solution and pouring the reaction product into petroleum, separates in red, prismatic crystals and decomposes at 101°. *4'-Iodoso-2 : 3'-dimethylazobenzene* is formed when the iodochloride is allowed to remain in contact with 20 per cent. sodium hydroxide solution for 8 days. It is an amorphous, reddish-yellow powder, which decomposes at 273° and is soluble in alcohol, more easily so in glacial acetic acid. *4'-Iodoxy-2 : 3'-dimethylazobenzene*, $C_6H_4Me \cdot N_2 \cdot C_6H_3Me \cdot IO_2$, is formed by the action of sodium hypochlorite solution on the iodochloride. It crystallises in prisms, melts at 180°, and explodes if rapidly heated in a capillary tube.

Phenyl-2 : 3'-dimethylbenzeneazophenyl-4'-iodonium chloride,

$$C_6H_4Me \cdot N_2 \cdot C_6H_4Me \cdot IPhCl,$$

is obtained by the action of mercury diphenyl on dimethylazobenzene iodochloride in benzene solution. It forms a powder consisting of small, scarlet needles, melts at 146°, and is soluble in water, alcohol, and ether. From this iodonium chloride, the following salts have been prepared. The *bromide* crystallises in red needles and melts and decomposes at 146°. The *iodide* crystallises in microscopic needles and melts at 143°. The *platinichloride*,

$$(C_6H_4Me \cdot N_2 \cdot C_6H_3Me \cdot IPhCl)_2PtCl_4,$$

crystallises in small, yellow leaflets and decomposes at 168°. The *dichromate* crystallises in small, scarlet needles and melts and decomposes at 178°.

*Di-*m*-bromophenyliodonium hydroxide*, $I(C_6H_4Br)_2 \cdot OH$, is obtained by the action of silver oxide on *m*-bromoiodobenzene. The following salts have been prepared. The *chloride* crystallises in slender needles and melts at 207° ; the *bromide* forms small needles and melts at 178° ; the *iodide* crystallises in slender needles and melts at 154°; the *platinichloride* separates from alcohol in glistening leaflets and melts and decomposes at 178° ; the *dichromate* crystallises in yellow needles and decomposes at 181°.

*Phenyl-*m*-bromophenyliodonium hydroxide*, $C_6H_4Br \cdot IPh \cdot OH$, is slightly alkaline in aqueous solution ; the *chloride* forms white needles and melts at 191° ; the *bromide* crystallises in needles and melts at 169° ; the *iodide* crystallises in needles and melts at 146° ; the *platinichloride* forms a yellow, crystalline precipitate and melts and decomposes at 181° ; the *mercurichloride* crystallises in white needles and melts at 130°; the *dichromate* is a yellow, crystalline powder, which melts and decomposes at 137°.

In aqueous solution, m-*bromophenyl-*p*-tolyliodonium hydroxide* has a slight alkaline reaction ; the *chloride* crystallises in small needles and melts at 174·5°; the *bromide* crystallises in white needles and melts at 175°; the *iodide* forms yellow needles and melts and decomposes at 139°. The *platinichloride* crystallises in yellow needles and melts and decomposes at 182·5° ; the *mercurichloride* forms white needles and melts at 139°.

m-*Bromophenyl-*o*-tolyliodonium hydroxide* is only known in its slightly alkaline, aqueous solution ; the *chloride* is a yellow, crystalline powder which melts at 170° ; the *bromide* is a white, crystalline precipitate which melts at 185°; the *platinichloride* crystallises in yellow leaflets and melts and decomposes at 182° ; the *mercurichloride*

melts at 110—115°; the *nitrate* is a white, crystalline precipitate which melts and decomposes at 181°.

m-*Bromophenyl-a-naphthyliodonium hydroxide* has a slight alkaline reaction in aqueous solution; the *chloride* forms small, white needles and melts at 159°; the *bromide* crystallises in small needles and melts at 156°; the *iodide* is a crystalline powder of small needles and melts and decomposes at 133°; the *platinichloride* crystallises in golden needles and melts at 158°; the *mercurichloride* crystallises in prisms and melts at 278°; the *dichromate* forms a powder of small, yellow needles and melts and decomposes at 132°. G. Y.

Action of Diazobenzene Chloride on Diphenylamine. LÉO VIGNON and ADOLPHE SIMONET (*Compt. rend.*, 1904, **138**, 1104—1105). —*Phenyldiazoaminobenzene*, $NPh{:}N{\cdot}NPh_2$, prepared by diazotising aniline hydrochloride in the presence of diphenylamine, is insoluble in water, sparingly soluble in alkaline solvents, readily so in alcohol, ether, or benzene, crystallises in bright yellow spangles from alcohol and water, melts at 47°, decomposes slowly at the ordinary temperature, rapidly at 100°, and explosively at 175—180°. It is readily decomposed by acids into nitrogen, diphenylamine, and phenol, and converted into the corresponding aminoazo-compound when heated with excess of diphenylamine and a little diphenylamine hydrochloride. The *hydrochloride* is violet, melts with decomposition at 135°, decomposes in the air, and is dissociated in water. The *platinichloride* decomposes without melting at 100—105°. M. A. W.

[Azo-derivatives of Phenylanthranilic Acid.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 150469).—Benzeneazodiphenylamine-*o*-carboxylic acid (this vol., i, 353) may also be regarded as benzeneazophenylanthranilic acid. Unlike phenylanthranilic acid, it does not yield an acridone derivative when heated with fuming sulphuric acid at 90—95°, but forms a *sulphonic acid*, which is yellow, dissolves in water, and forms yellow salts. Similar dyes are obtained from toluene-*o*-azo-*o*-tolylanthranilic acid (toluene-*o*-azo-*o*-tolylphenylamine-*o*-carboxylic acid) and toluene-*p*-azo-*p*-tolylanthranilic acid.

C. H. D.

Diazoamino-compounds. LOUIS MEUNIER (*Bull. Soc. chim.*, 1904, [iii], **31**, 641—644).—5 : 5′-*Dinitro*-2 : 2′-*diazoaminotoluene*, produced by the action of sodium nitrite (1 mol.) on 5-nitro-*o*-toluidine dissolved in acetic acid, separates from acetone in golden-yellow crystals and melts at 237°.

The three *diazoaminobenzenedisulphonic acids* were prepared by dissolving the corresponding anilinedisulphonic acids (2 mols.) in water containing sodium carbonate (1 mol.) and adding to this sodium nitrite (1 mol.) and sulphuric acid ($\frac{1}{2}$ mol.). The *sodium* salts so formed were obtained as greenish-yellow, hygroscopic precipitates by the addition of ammonium chloride. They react with copper powder to form *cuprous* derivatives which produce red solutions in water and have the formula $SO_3Na{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NCu{\cdot}C_6H_4{\cdot}SO_3Na$. Solutions of

these cuprous derivatives in water give with barium chloride a red *precipitate* having the constitution $\begin{array}{l}SO_3\text{——}Ba\text{——}SO_3 \\ \mid \qquad\qquad\qquad\quad \mid \\ C_6H_4{\cdot}N{:}N{\cdot}NCu{\cdot}C_6H_4\end{array}$.

The *sodium* and *barium* salts of o-*diazoaminotoluene*-p-*disulphonic acid* were also prepared by the above method; they closely resemble the similar salts of the lower homologue. T. A. H.

Diazoaminomagenta and Diazoaminorosaniline. Louis Pelet and W. Redard (*Bull. Soc. chim.*, 1904, [iii], 31, 644—646).—When a solution of nitrous acid, prepared by acidifying an aqueous solution of potassium nitrite, is added to excess of a solution of magenta in water, there is formed in solution in addition to diazomagenta, *diazoaminomagenta*, $CCl{<}\begin{array}{l}C_6H_3Me{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_3Me \\ (C_6H_4\text{——}N{:}N{\cdot}NH{\cdot}C_6H_4)_2\end{array}{>}CCl$.

When sodium carbonate is added to the liquid so produced, a brown precipitate of *bisdiazoaminorosaniline*,

$$OH{\cdot}C_6H_4{\cdot}C(OH){<}\begin{array}{l}C_6H_3Me{\cdot}N{:}N{\cdot}NHC_6H_3Me \\ C_6H_4\text{——}N{:}N{\cdot}NH\text{——}C_6H_4\end{array}{>}C(OH){\cdot}C_6H_4{\cdot}OH,$$

is formed. This is soluble in a solution of sodium hydroxide, and when dried at 105° loses 4 mols. of water and passes very readily into rosolic acid. T. A. H.

Dyes containing Aminoarylacyl or Aminoarylaminoacyl Groups. Gesellschaft für Chemische Industrie in Basel (D.R.-P. 151017).—The chlorides of nitro- or acetylamino-aromatic acids may be combined with aminonaphtholsulphonic acids, and the products reduced or hydrolysed, forming aminoarylacylaminonaphtholsulphonic acids. When the alkali salts of these acids are combined with diazonium salts, the diazo-group enters the aminonaphthol residue, and the resulting azo-compound therefore contains a diazotisable amino-group in the aminoarylacyl residue. The dyes obtained by diazotising such compounds and combining with β-naphthol, *m*-tolylenediamine, &c., are bright orange or red in colour, unlike the corresponding compounds from aminonaphtholsulphonic acids, which are dark blue or black. A number of dyes of this class are enumerated in the patent. C. H. D.

Ritthausen's Classification of Vegetable Proteids. Dmitri Prianischnikoff (*Landw. Versuchs-Stat.*, 1904, 60, 15—27).—The following grouping of proteids is proposed: (1) water-soluble proteids (for example, Osborn's leucosin); (2) proteids insoluble in water, but soluble in salt solutions (Osborn's edestin and Ritthausen's legumin); (3) proteids soluble in 70 to 80 per cent. alcohol and precipitated in small quantity by sodium chloride (gliadin); (4) proteids rich in phosphoric acid and insoluble in the above solvents, but dissolved by alkali and precipitated by acids (Ritthausen's gluten-casein = Osborn's and Fleurent's glutenin).

In addition to the true proteids, substances of lower mol. wt. (albumose and peptones) and substances of greater mol. wt. (nucleoproteids) occur in plants.

The following table shows the relations of vegetable proteids and their derivatives to solvents:

	Dilute alcohol.	Water at 100°.	Cold water.	10 °/₀ NaCl.	Pan-creatic juice.	KOH	No. of positive signs.
1. Peptone and albumoses	+	+	+	+	+	+	6
2. Albumin ...	−	−	+	+	+	+	4
3. Globulin ...	−	−	−	+	+	+	3
4. Gliadin ...	+	−	−	−	+	+	3
5. Casein ...	−	−	−	−	+	+	2
6. Nuclein ...	−	−	−	−	−	+	1

N. H. J. M.

White and Yoke of Egg; Action of Hydrogen Sulphide on Unbroken Eggs. Egidio Pollacci (*Gazzetta*, 1904, 34, i, 278—286). —By boiling white and yoke of egg separately with water, the author finds that they both lose a considerable proportion of their sulphur, showing that the proteids are broken down and the nutritive value of the egg diminished.

On allowing an unbroken egg to remain for 24 hours in a closed vessel full of hydrogen sulphide, it was found, on breaking the egg, that the white had lost its natural viscosity and had become limpid like water, and that it had assumed a yellowish-green colour and a fœtid odour; the yolk, on the other hand, had become of a very dark chocolate colour. The albuminates, especially those of sodium and calcium, present in the white are hence decomposed into the corresponding sulphides, together with mercaptan-substances; the dark colour of the yolk is due to the formation of ferric sulphide.

The reactions of the white and yolk of egg are given in tabular form.

T. H. P.

Constitution of the Indole Group in Albumin. (Synthesis of the so-called Scatolecarboxylic Acid.) Source of Kynurenic Acid. Alexander Ellinger (*Ber.*, 1904, 37, 1801—1808).—The decomposition products from proteids which contain the indole grouping are, besides indole itself, scatole, scatolecarboxylic acid, and scatoleacetic acid; to the two latter substances, the formulæ,

$$C_6H_4{<}{}^{CMe}_{NH-}{>}C\cdot CO_2H \text{ and } C_6H_4{<}{}^{CMe}_{NH-}{>}C\cdot CH_2\cdot CO_2H$$

respectively have been assigned by Nencki and others, whilst to the parent substance, tryptophan, the formula for α-amino-α-scatoleacetic acid, $C_6H_4{<}{}^{CMe}_{NH-}{>}C\cdot CH(NH_2)\cdot CO_2H$, has been given (compare Hopkins and Cole, Abstr., 1902, i, 193). Wislicenus and Arnold have, however, synthesised scatolecarboxylic acid of the constitution $C_6H_4{<}{}^{CMe}_{NH-}{>}C\cdot CO_2H$, and this substance is not identical with that obtained from proteids. On this ground, and also from the results of biological experiments conducted by the author and Gentzen (Abstr.,

1903, i, 781), the constitution of scatolecarboxylic acid has been studied afresh and is shown to be $C_6H_4<\underset{NH}{\overset{C(CH_2\cdot CO_2H)}{}}>CH$.

Itaconic acid was converted into aconic acid (Metzing, *Inaug. Diss.*, Königsberg, 1901), which, on being boiled with water, yielded β-aldehydopropionic acid (von Ungern-Sternberg, *Inaug. Diss.*, Königsberg, 1904. Compare also Perkin and Sprankling, *Trans.*, 1899, 75, 11). The latter was then converted by the silver salt method into its methyl ester, the phenylhydrazone of which, when boiled for several hours with alcoholic sulphuric acid, yielded *methylindole*-3-*acetate*, thus:

$$C_6H_5\cdot N_2H\colon CH\cdot CH_2\cdot CH_2\cdot CO_2Me = C_6H_4<\underset{NH}{\overset{C(CH_2\cdot CO_2Me)}{}}>CH + NH_3.$$

The acid obtained from the hydrolysis of this ester was identical in melting point and crystalline form with that prepared by E. and H. Salkowski from proteids.

Physiological experiments on dogs showed that tryptophan is converted in the organisms into kynurenic acid. Since the latter has been shown by Camps (Abstr., 1901, i, 751) to be 4-hydroxyquinoline-3-carboxylic acid, $C_6H_4<\underset{N=\!=\!=CH}{\overset{C(OH)\cdot C\cdot CO_2H}{}}$, the formula for tryptophan is most probably $NH<\underset{CH}{\overset{C_6H_4}{}}>C\cdot CH(CO_2H)\cdot CH_2\cdot NH_2$.

A. McK.

The Carbohydrate Group in Serum-globulin, Serum-albumin, and Egg-albumin. Emil Abderhalden, Peter Bergell, and Theodor Dörpinghaus (*Zeit. physiol. Chem.*, 1904, 41, 530—534).—Serum-globulin yields a very small quantity (about 0·1 per cent.) of dextrose, identified by its osazone; whether traces of glucosamine are also present is doubtful. Whether the serum-globulin really contains a dextrin-like substance in its molecule which yields the sugar is uncertain; the variable amount of sugar obtained rather points to an admixture. Serum-albumin similarly yields a small amount of sugar, but after repeated crystallisation there is no evidence of any at all. The small amount of reducing material obtained from egg-albumin is glucosamine; its amount is variable. Here also mechanical admixture is the probable explanation of its presence. W. D. H.

Organic Chemistry.

Optical Investigation of Naphtha and of its Distillation Products. M. A. Rakusin (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 554—559).—The author's measurements show that both the colourless and the yellow distillates obtained from naphtha give rotations varying from +0·2 to +2·3 divisions of the Soleil-Ventzke scale in a tube 200 mm. long, the highest value being given by yellow cylinder oil from Baku naphtha. "Benzine" and petroleum from Grosny naphtha and also the yellow American cylinder oil "Viscolite" (of the Vacuum Oil Company) exhibit dextro-rotations. T. H. P.

$\alpha\gamma$-Pentadiene. N. Wosnesensky (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 532—536).—$\beta\delta$-Dibromopentane (see Poray-Koschitz, this vol., i, 363) loses its bromine when treated with quinoline, yielding *$\alpha\gamma$-pentadiene*, $CHMe\colon CH\cdot CH\colon CH_2$, which is a mobile liquid with a characteristic odour, boils at 41·5—43°, and has sp. gr. 0·6952° at 0°/0°. The corresponding *tetrabromide*, $C_5H_8Br_4$, crystallises from alcohol in shining plates melting at 114°. Oxidation of the pentadiene with permanganate gives rise to acetic acid. T. H. P.

Decomposition of Ethylene and Ethylidene Dichlorides by Heat. Heinrich Biltz and Ernst Küppers (*Ber.*, 1904, 37, 2398—2423. Compare Abstr., 1903, i, 1).—The decomposition of ethylene and ethylidene dichlorides into chloroethylene and hydrogen chloride takes place at 300—450° under the catalytic action of the glass walls of the reaction vessel. At 300—400°, the dichlorides are in varying equilibrium with their decomposition products, the amount of the latter formed increasing with the rise in temperature, but also varying with the extent of surface of the glass vessel. Above 400°, the decomposition takes place completely.

One glass vessel was found to have no catalytic action, as with the dichlorides at 401° for 120 minutes, and at 448° for 60 minutes, no increase of pressure was observed. G. Y.

Action of the Simplest Secondary Iodide on Magnesium. Wladimir Tschelinzeff (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 549—554).—When magnesium and *iso*propyl iodide interact, besides the normal formation of organo-magnesium compound, there takes place also a reaction of elimination and reduction, thus: $2CHMe_2I + Mg = MgI_2 + CH_2\colon CHMe + CH_2Me_2$, propane and propylene being formed. This reaction accounts for about 41 per cent. of the *iso*propyl iodide, whilst 1·47 per cent. undergoes the following decomposition: $2CHMe_2I + Mg = MgI_2 + 2CH_2\colon CHMe + H_2$. T. H. P.

Preparation of Alcohol from Acetylene. La Société S. Jay & Co. (D.R.-P. 149893).—A mixture of 1 vol. of acetylene with 4 vols. of hydrogen is passed into a specially constructed apparatus of glass

or porcelain, and is there mixed with ozonised oxygen, the whole being cooled by means of solid carbon dioxide. Combination readily takes place, with the formation of alcohol, inactive oxygen escaping through a mercury outlet. A suitable form of apparatus is described and figured. C. H. D.

Preparation of Primary Alcohols by means of the Corresponding Acids. LOUIS BOUVEAULT and GUSTAVE BLANC (*Bull. Soc. chim.*, 1904, [iii], 31, 748—750. Compare Abstr., 1903, i, 597 and 673).—The method of reduction previously described (*loc. cit.*) is found to be applicable to substituted acetic acids of the types $CHRR^{I}\cdot CO_2H$ and $CRR^{I}R^{II}\cdot CO_2H$.

α-Methyloctoic acid, prepared from octoic acid obtained from castor oil, boils at 136° under 17 mm. pressure and has a sp. gr. 0·9098 at 0°/4°. The ethyl ester has a fruity odour, boils at 99° under 13 mm. pressure, has a sp. gr. 0·8759 at 0°/4°, and on reduction furnishes α-methyloctyl alcohol, a liquid of pleasant odour, boiling at 98—99° under 16 mm. pressure and having a sp. gr. 0·8418 at 0°/4°.

Ethyl αα-dimethylbutyrate is a liquid of pleasant, slightly camphoraceous odour; it boils at 141—142°, has a sp. gr. 0·883 at 0°/4°, and on reduction furnishes αα-dimethylbutyl alcohol. The latter has a camphoraceous odour, boils at 135°, does not solidify when cooled to −15°, and has a sp. gr. 0·844 at 0°/4°.

Ethyl campholate, $\begin{matrix} CHMe\cdot CMe_2 \\ | \qquad\qquad \\ CH_2 \text{——} CH_2 \end{matrix}\!\!>\!CMe\cdot CO_2Et$, on reduction furnishes a *campholyl alcohol*, which has an odour similar to that of borneol, crystallises in white needles, melts at 60°, and boils at 213° (compare Errera, Abstr., 1893, 108; 1894, 202); the *phenylurethane* melts at 45° and is readily soluble in organic solvents. T. A. H.

Methyl*iso*butylallylcarbinol. DIMITRI MARKO (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 544—549).—*Methyl*iso*butylallylcarbinol*,

$$C_4H_9\cdot CMe(C_3H_5)\cdot OH,$$

prepared by decomposing with water the compound obtained by the action of zinc and allyl iodide (2 mols.) on methyl*iso*butyl ketone (1 mol.), is a colourless liquid with a caustic taste and a faint odour of turpentine; it boils at 173·7°, is readily soluble in alcohol or ether, does not crystallise even at −25°, and has the sp. gr. 0·83545 at 20°/0°, 0·83652 at 20°/20°, 0·82632 at 30°/0°, and 0·82748 at 30°/30°. Its *acetyl* derivative was prepared and analysed. On oxidation with permanganate, methyl*iso*butylallylcarbinol yields: (1) *αβδ-trihydroxy-δζ-dimethylheptane*, $CHMe_2\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, which is an uncrystallisable, syrupy liquid soluble in water, alcohol, or ether; a mixture of its diacetyl and triacetyl derivatives was prepared. (2) *β-Hydroxy-βδ-dimethylhexoic acid*,

$$CH_3\cdot CHMe\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CO_2H,$$

was obtained as a thick, uncrystallisable syrup soluble in water, alcohol, or ether; its *calcium*, *silver*, and *zinc* salts were prepared and analysed.

All the methylbutylallylcarbinols are now known, their boiling points and sp. grs. being as follows:

Methylbutylallyl-carbinol with	B. p. at 760 mm. pressure.	Sp. gr. at 20°/0°.	Sp. gr. at 20°/20°.
n-Butyl	179·1°	0·84412	0·84497
*iso*Butyl	173·7	0·83545	0·83652
sec.-Butyl	174·9	0·85438	0·85526
tert.-Butyl	168·4	0·85535	0 85639

T. H. P.

Syntheses of Amylene αε-Glycol, of the Nitrile, and of Pimelic Acid. JULES HAMONET (*Compt. rend*, 1904, 139, 59—61. Compare Abstr., 1901, i, 187, 247; this vol., i, 467).—*αε-Diacetoxypentane*,

$$OAc\cdot[CH_2]_5\cdot OAc,$$

is a colourless liquid with a fruity odour, which boils at 241° under 760 mm. pressure, when placed in a freezing mixture, forms white crystals melting at 2°, has a sp. gr. 1·021 at 18°, and yields, on saponification, *amylene αε-glycol*, $OH\cdot[CH_2]_5\cdot OH$, in the form of a thick liquid resembling glycerol; this has a burning and bitter taste, boils at 238—239° under 760 mm. or at 155° under 31 mm. pressure, has a sp. gr. 0·994 at 18°, and solidifies, but does not crystallise, in a mixture of solid carbon dioxide and ether. *Pimelonitrile*,

$$NC\cdot[CH_2]_5\cdot CN,$$

prepared by the action of potassium cyanide on di-iodopentane at 85°, is a mobile liquid, which boils at 175—176° under 14 mm. pressure, has a sp. gr. 0·949 at 18°, does not solidify in a mixture of solid carbon dioxide and ether, and yields pimelic acid when heated in a sealed tube with concentrated hydrochloric acid at 100°. M. A. W.

Action of Sulphuric Acid on Certain Glycerols obtained by the Oxidation of Unsaturated Tertiary Alcohols of the Series $C_nH_{2n-1}OH$, containing One Allyl Radicle. DMITRI WAGNER, VIKTOR LWOW, and ALEXANDR BENING (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 539—544. Compare Petchnikoff, Abstr., 1901, i, 183, and 1902, i, 338).—The authors have isolated the alcohol oxides formed by the action of dilute sulphuric acid on hydroxymethylethylallylcarbinol, dihydroxymethylpropylallylcarbinol, and dihydroxymethyl *n*-butylallylcarbinol. The three *compounds* obtained, which have the formulæ $C_7H_{14}O_2$, $C_8H_{16}O_2$, and $C_9H_{18}O_2$ respectively, are colourless liquids moderately soluble in water, alcohol, or ether; their constants are as follows:

	Boiling point (corr.).	Difference.	Sp. gr. at 0°/0°.	Sp. gr. at 20°/0°.
$C_7H_{14}O_2$	204·5°		1·00076	0·98677
		15·5°		
$C_8H_{16}O_2$	220·0		0·99413	0·97968
		14·8		
$C_9H_{18}O_2$	234·8		0·95910	0·95910

T. H. P.

Method of Characterising the Fatty Acids. René Locquin (*Compt. rend.*, 1904, 138, 1274—1276).—The method consists in converting the fatty acid, $R{\cdot}CO_2H$, by means of chloroacetone into the ketonic ester, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2R$, and transforming this into the corresponding semicarbazone. The theoretical quantity of sodium is added to the acid (1 mol.) dissolved in anhydrous ether, and chloroacetone (1 mol.) is then added. After evaporating off the ether, the residue is heated at 120—130°, when the reaction $CH_3{\cdot}CO{\cdot}CH_2Cl + R{\cdot}CO_2Na = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2R + NaCl$ takes place. After separation of the ester, it is treated with semicarbazide in acetic acid solution. The semicarbazones derived from the various fatty acids crystallise well and can be readily recognised. H. M. D.

Some Cuprous Salts. Alexandre Joannis (*Compt. rend.*, 1904, 138, 1498—1500. Compare Abstr., 1903, ii, 371).—The author has prepared the cuprous salts of formic and benzoic acids by allowing the ammonium salt of the acid dissolved in liquid ammonia to react with cuprous oxide in a sealed apparatus from which all air and moisture have been removed. The cuprous salt is recrystallised from liquid ammonia, and the crystals washed with the same solvent until a compound of constant composition is obtained. *Cuprous formate*, $Cu_2(CHO_2)_2,4NH_3,\frac{1}{2}H_2O$, is a pale blue substance, which becomes deep blue in contact with moist air and brownish-black in dry air; it is decomposed by dilute acids, giving yellow cuprous oxide. *Cuprous benzoate*, $Cu_2(PhCO_2)_2,5NH_3$, is a bluish-white, crystalline substance, very unstable in air. M. A. W.

Auto-hydrolysis of Crude Animal Fats. Peter Pastrovich (*Monatsh.*, 1904, 25, 355—364. Compare Abstr., 1903, ii, 249).—In an emulsion of crude tallow with water at 35°, the fat is hydrolysed by the proteid present in the membrane which surrounds the tallow. The presence of this membrane together with water increases the acid number to a considerable degree; the increase is much greater with 10 per cent. than with 5 per cent. of membrane. The auto-hydrolysis of tallow is diminished by the presence of small quantities of mineral acids or a 2 per cent. solution of chloral hydrate, and is almost completely stopped by addition of a 2 per cent. solution of mercuric chloride. Traces of ammonia or alkali hydroxides favour, but larger quantities diminish, the hydrolysis.

The increase of the acid number is found to differ with various parts of the tallow, and to be greatest for that part which contains most olein. It is also affected by the addition of other fats.

G. Y.

[Iodochlorides of Oleic Acid and its Analogues.] Aktiengesellschaft für Anilin-Fabrikation (D.R.-P. 150434).—It is not possible to prepare salts of iodo-fatty acids by the saponification of the iodine derivatives of fats, on account of the removal of iodine. Oleic and other unsaturated fatty acids, however, combine readily with iodine chloride, and the acids thus obtained readily form solid salts with inorganic bases, containing 10—25 per cent. of iodine.

These salts are almost tasteless, and find therapeutic application. The patent contains details of the preparation of a number of salts of chloroiodo-fatty acids. C. H. D.

Method of Resolving Fermentation Lactic Acid into its Optically Active Components. ÉMILE JUNGFLEISCH (*Compt. rend.*, 1904, 139, 56—59).—Ordinary quinine lactate of commerce is obtained by dissolving in its own weight of 70 per cent. alcohol a mixture of fermentation lactic acid and its equivalent of quinine; the product consists of crystalline needles of the racemic lactate containing H_2O. If, however, these crystals are left in contact with the mother liquor in a closed vessel, they slowly disappear, and octahedral crystals are formed; these are removed and the residue similarly treated. The octahedral crystals consist of quinine *d*-lactate; the *l*-lactate remains in solution and can be isolated in the form of long, silky needles containing $\frac{1}{2}H_2O$. Quinine *d*-lactate is dimorphous, crystallising in slender needles from hot concentrated solutions, or in octahedral crystals from warm or cold solutions; the needles change into the octahedral form at the ordinary temperature, whilst the converse change takes place if the octahedral crystals are heated at 150°. Wyrouboff has determined the crystallographical constants of the octahedral crystals; they are pseudo-quadratic [$a : c = 1 : 1{\cdot}8103$]. The quinine lactate prepared from the lactic acid extracted from meat juice is identical with the quinine *d*-lactate prepared as above.
M. A. W.

Action of Iodine on Dehydroacetic Acid in Pyridine Solution. GIOVANNI ORTOLEVA and G. VASSALLO (*Gazzetta*, 1904, 34, i, 342—347. Compare Abstr., 1902, i, 54, 674, and Abstr., 1903, i, 851).—The action of iodine on a pyridine solution of dehydroacetic acid mixed with alcohol yields two new compounds.

(1) A *compound*, $C_{13}H_{14}O_4NI$, which crystallises from water in shining, grey scales melting and decomposing at 234°; it is slightly soluble in acetic acid or acetic anhydride, and more so in concentrated hydrochloric acid, from which it crystallises unchanged; the addition of silver nitrate to its aqueous solution precipitates the whole of the iodine; concentrated sulphuric acid decomposes it with elimination of iodine and hydriodic acid, whilst when heated with moist oxide of silver, the silver is deposited in the form of a mirror; dilute aqueous solutions of alkali hydroxides or carbonates colour it yellow in the cold, but when heated they dissolve it, giving red solutions, from which it is in great part precipitated unaltered by the addition of sulphuric acid. If, however, it is dissolved in warm 50 per cent. potassium hydroxide solution, which is then, cautiously and with cooling, acidified with dilute sulphuric acid, two substances are obtained: (*a*) a *compound*, $C_{21}H_{19}O_8N$, crystallising from water in shining, white scales, which begin to darken at 220°, and are completely carbonised without melting at 270°; with ferric chloride, its aqueous solution gives a violet coloration. (*b*) A small quantity of a substance melting at 189—190°, which is probably the triacetic acid obtained by Collie (Trans., 1891, 59, 617).

(2) A *compound*, $C_{16}H_{14}O_8$, which crystallises from a mixture of chloroform and benzene in small tufts of long, white needles, soluble in acetic acid, and melting and decomposing at 214—215°; it dissolves in potassium hydroxide solution with formation of a reddish-violet coloration, and, on heating the liquid, it decomposes with evolution of acetone; its aqueous solution has a faint acid reaction and readily decolorises permanganate. With bromine in chloroform solution, it yields a *bromide* which melts and decomposes at 153—154° and decolorises permanganate; nitrate of silver removes the bromine from it. T. H. P.

Preparation of α-Mono-substituted Acetoacetic Esters RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 757—760. Compare Abstr., 1901, i, 311; 1902, i, 704; 1903, i, 63, 142, and this vol., i, 552).—The author draws attention to the precautions which must be observed in the preparation of these esters in order to ensure a good yield.

Ethyl *iso*amylacetoacetate, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2Et$, now obtained for the first time in a pure state by the use of synthetic *iso*amyl iodide (compare this vol., i, 546), is a mobile liquid which boils at 114—115° under 12 mm. pressure and has a sp. gr. 0·957 at 0°/4°.

Ethyl sec.-*octylacetoacetate*, $C_6H_{13}{\cdot}CHMe{\cdot}CHAc{\cdot}CO_2Et$, obtained by the use of *sec.*-octyl iodide, prepared by Bouïs' method (*Ann. Chim. Phys.*, 1855, [iii], 44, 128) from the octyl alcohol of castor oil, is a slightly viscous liquid which boils at 152° under 17 mm. pressure and has a sp. gr. 0·944 at 0°/4°. T. A. H.

Preparation of Stearolactone. ALEXIS A. SHUKOFF (D.R.-P. 150798).—Stearolactone is obtained by the action of sulphuric acid on oleic, *iso*oleic, elaidic, sulphostearic, and hydroxystearic acids, or mixtures of such acids, when at least 1 mol. of concentrated sulphuric acid is employed for each mol. of oleic acid at a temperature of 60—90°. C. H. D.

Camphocarboxylic Acid, its Salts, Esters, and Ester Salts. JULIUS W. BRÜHL and H. SCHRÖDER (*Ber.*, 1904, 37, 2512—2524).—The following results were obtained in a series of physical chemical measurements on camphocarboxylic acid, its salts, esters, and ester salts. Molecular weight determinations show camphocarboxylic acid to be largely bimolecular in benzene and ethereal solutions, unimolecular, however, in methyl alcohol and water. Its esters are unimolecular, not only in benzene and alcohol, but also in the solid state, whilst the sodium salts of methyl and ethyl camphocarboxylate are ter- or quadri-molecular in benzene and ether, actually ionised, on the other hand, in methyl alcohol. In benzene or ethereal solution, neither camphocarboxylic acid nor its salts nor ester salts behave as electrolytes. In methyl alcohol, however, the sodium salts of both camphocarboxylates and methyl camphocarboxylate behave normally as electrolytes. The rate of the autohydrolysis of the ester salts in aqueous solution has been investigated; in absolute methyl alcohol, however, the ester remains unchanged. E. F. A.

Products of Decomposition of Bromosuccinic Acid and its Salts in Aqueous Solution. Wolf J. Müller and F. Suckert (*Ber.*, 1904, 37, 2598—2604).—Malic and fumaric acids were estimated by weighing the dry barium salts from a known weight of bromosuccinic acid; the excess of weight above that calculated for barium fumarate represented the additional water contained in the malate, the weight of which could thus be calculated.

The percentage of fumaric acid increased with the concentration, although not according to a linear law, with the proportion of hydrochloric acid added as catalyst, and with the concentration of the bromosuccinic acid; the proportion of fumaric acid also showed a marked increase when the temperature was raised to 100°. Thus the percentage of fumaric acid from $N/20$ bromosuccinic acid was 9·57 at 75° and 11·33 at 100°, but 17·61 and 19·45 in presence of $N/10$ HCl at 75° and 100° respectively. The salts of bromosuccinic acid give only malic acid when hydrolysed, and no fumaric acid. T. M. L.

New Synthesis of αα-Dimethyladipic Acid. Gustave Blanc (*Compt. rend.*, 1904, 139, 65—67).—In addition to the synthesis of αα-dimethyladipic acid already given (compare this vol., i, 369), the author has synthesised it from αα-dimethyl-γ-butyrolactone by the following method. The lactone was converted by the action of phosphorus pentabromide and subsequent treatment with alcohol into ethyl γ-bromo-αα-dimethylpropionate, $CO_2Et\cdot CMe_2\cdot CH_2\cdot CH_2Br$, boiling at 100° under 10 mm. pressure and condensing with the sodium derivative of ethyl cyanoacetate to give ethyl δ-cyano-αα-dimethyl adipate, $CO_2Et\cdot CMe_2(CH_2)_2\cdot CH(CN)\cdot CO_2Et$, boiling at 205—210° under 15 mm. pressure and on hydrolysis with alcoholic potash yielding the acid, $CO_2H\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH(CO_2H)_2$, melting at 167—168° already obtained by oxidising dihydro*iso*lauronic acid (compare Abstr., 1900, i, 329); this acid loses CO_2 on heating at 180°, and is quantitatively converted into αα-dimethyl adipic acid melting at 87—88°. The αα-dimethyl-γ-butyrolactone used in this synthesis was obtained by reducing αα-dimethylsuccinic anhydride with sodium and alcohol and is identical with the compound obtained by Blaise (Abstr., 1903, i, 604) from β-iodo-αα-dimethylglutaric acid.

In view of these facts, the author suggests that the lactone, boiling at 207°, obtained by Perkin (compare Trans., 1901, 81, 257) by heating αα-dimethylglutaconic acid and treating the unsaturated acid thus obtained with dilute sulphuric acid is *iso*hexolactone, which boils at 207°, and not αα-dimethyl-γ-butyrolactone as stated. M. A. W.

Hæmatin. William Küster and Karl Haas (*Ber.*, 1904, 37, 2470—2473. Compare Abstr., 1902, i, 845).—*α-Methyl-β propylmaleic anhydride*, $C_8H_{10}O_3$, prepared by combining hydrogen cyanide with cooled ethyl propylacetoacetate, hydrolysing, and distilling the methylpropylmalic acid obtained, is purified by fractional distillation or by means of the barium salt, and forms a mobile, slightly yellow, highly refractive liquid boiling at 241—242° (corr.), and has a sp. gr. 1·098 at 15°. It is almost insoluble in cold water, but dissolves

readily in alcohol, ether, chloroform, benzene, or ethyl acetate. The *barium* salt, $C_8H_{10}O_4Ba,H_2O$, forms pearly leaflets.

Alcoholic ammonia at 130° converts it into the *imide*, $C_8H_{11}O_2N$, crystallising from dilute ammonia after repeated treatment with animal charcoal in long, silky-white needles, and melting at 56—57° and subliming without decomposition. It dissolves readily in organic solvents, sparingly in water. Its odour resembles that of iodoform.

The oxidation of hæmopyrrole (Nencki and Zalesky, Abstr., 1901, i, 434) yields an imide melting at 63—64° and having the odour of iodoform, decomposing more readily than the synthetic imide; it may perhaps be an isomeride.

Methylisopropylmaleimide melts at 44—45° and closely resembles the *n*-propyl compound in appearance and odour. A third isomeride, xeronimide, is under investigation. C. H. D.

Ethylmalic Acid. FRITZ FICHTER and MAX GOLDHABER (*Ber.*, 1904, 37, 2382—2384).—*Ethyl ethylmalate*,

$$CO_2Et\cdot CHEt\cdot CH(OH)\cdot CO_2Et,$$

prepared by reducing ethyl oxalacetate with aluminium in moist ethereal solution, boils at 133—135° under 12 mm. pressure. The *acid*, $C_6H_{10}O_5$, crystallises from a mixture of ether and light petroleum in colourless prisms and melts at 133—134°. *Ethylmalanil*,

$$\begin{matrix} CHEt\text{---}CO \\ | \\ CH(OH)\cdot CO \end{matrix}\!\!>\!NPh,$$

crystallises from water in colourless, flaky needles and melts at 142—143°. *Ethylmalanilide*, $\begin{matrix} CHEt\cdot CO\cdot NHPh \\ | \\ CH(OH)\cdot CO\cdot NHPh \end{matrix}$, is insoluble in water, crystallises from alcohol in minute needles, and melts at 203—204°. *a-Ethylumbelliferone*, $HO\cdot C_6H_3\!<\!\begin{matrix} CH\!:\!CEt \\ \quad\ \ | \\ O\text{---}CO \end{matrix}$, prepared by condensing the acid with resorcinol and sulphuric acid, crystallises from water in minute, white, glistening needles, melts at 123—124°, gives blue, fluorescent solutions, and reduces Fehling's and ammoniacal silver solutions. Dry distillation of the acid gave chiefly methylcitraconic acid.

Methylcitraconanil, $\begin{matrix} CEt\cdot CO \\ || \\ CH\text{—}CO \end{matrix}\!\!>\!NPh$, crystallises from alcohol or dilute acetic acid in pale yellow, felted needles and melts at 108—109°. The dibromide, *ethyldibromosuccinanil*, $\begin{matrix} CBrEt\cdot CO \\ | \\ CHBr\cdot CO \end{matrix}\!\!>\!NPh$, crystallises from acetic acid in colourless needles and melts at 164—165. *Anilinomethylcitraconanil*, $\begin{matrix} CEt\cdot CO \\ || \\ NHPh\cdot C\text{---}CO \end{matrix}\!\!>\!NPh$, crystallises from alcohol in glistening, yellow flakes and melts at 113—114°.

Small quantities of methylitaconic and methylmesaconic acids are also produced in the distillation of ethylmalic acid. T. M. L.

Product of the Spontaneous Change of Ethyl Oxalacetate. LOUIS J. SIMON (*Compt. rend.*, 1904, 138, 1505—1508).—A specimen

of ethyl oxalacetate which has been kept for a long time gives a violet coloration with an alkali hydroxide or with the alkali salt of a weak acid such as boric or formic. The reaction is not given by pure ethyl oxalacetate, either freshly prepared or regenerated from its copper derivative, but it is given by these specimens at the end of a certain time, and must, therefore, be due to a product of spontaneous change. An impure specimen of the colour-giving compound was obtained from the residue left after distilling off the pure ethyl oxalacetate from a commercial sample; it is an oily liquid boiling at 210—215°, and the result of analysis and molecular weight determination point to it being a condensation product of two molecules of ethyl oxalacetate with the loss of one molecule of alcohol,

$$CO_2Et\cdot CO\cdot CH(CO_2Et)\cdot CO\cdot CO\cdot CH_2\cdot CO_2Et.$$

It is, further, more readily prepared by the action of anhydrous zinc chloride on ethyl oxalacetate. Attempts to isolate the coloured product resulting from the action of alkali hydroxides on the condensation product were unsuccessful; by treating the latter compound with dilute alkali for several days, acidifying, and then extracting with ether, an oily substance was obtained after evaporating off the ether, which develops a deep blue colour in contact with alkalis, or even water or alcohol, but no pure compound could be obtained. The author suggests that the coloured compound may be a substituted dioxyquinone, $\begin{array}{l} CO_2Et\cdot CH\cdot CO\cdot CO \\ \qquad\qquad | \qquad\quad | \\ \qquad\quad CO{-}CO\cdot CH\cdot CO_2Et \end{array}$, formed from the colour-giving compound by the elimination of another molecule of alcohol.

M. A. W.

Stereochemical Notes [Pasteur's Method of Resolving by means of Active Compounds. Solubility of a Tartrate Compared with that of a Racemate]. WILHELM MEYERHOFFER (*Ber.*, 1904, **37**, 2604—2610).—In the case of double salts, there are three temperature intervals corresponding with (1) the crystallisation from solution of the separate salts, (2) the crystallisation of the less soluble salt followed by the double salt, (3) crystallisation of the double salt only. Pasteur's method is only applicable within the limits of the first two intervals.

The tension of the stable or labile tartrate mixture is double that of the single tartrate. The tension of a stable racemate may be smaller, or at most twice as great, whilst that of a labile racemate is more than twice as great as that of the tartrate. In an indifferent solvent, the tension curves have the same form as the solubility curves, and the figures given in the paper are applicable to either case. T. M. L.

Preparation of Methylenecitric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 150949).—Methylenecitric acid is best prepared by heating citric acid with chloromethyl alcohol at 130—140°. A yield of 80 per cent. is obtained. C. H. D.

Atmospheric Formaldehyde. H. HENRIET (*Compt. rend.*, 1904, **139**, 67—68. Compare this vol., i, 289).—Gautier has pointed out that 0·5 to 1 gram per 100 cubic metres is the highest proportion of

formaldehyde air can contain without ceasing to be respirable; the author therefore suggests that the large proportion (2—6 grams per 100 cubic metres) which he found experimentally may be present in the form of some compound such as methylal, from which formaldehyde is readily regenerated by the action of acids, for the amount of formaldehyde in water through which a large quantity of air has been bubbled is much increased by heating the water with dilute sulphuric or acetic acid. M. A. W.

New Method of Preparing Acetylenic Aldehydes; Action of Hydroxylamine. CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1904, 138, 1339—1341. Compare Abstr., 1901, i, 581).—The method of Bodroux (compare this vol., i, 250) and of Tschitschibabin (compare this vol., i, 221) can be applied to the preparation of the acetals of acetylenic aldehydes, $R\cdot C:C\cdot CH(OEt)_2$, from which the aldehyde is obtained by hydrolysis. For this purpose, molecular proportions of magnesium ethyl bromide or iodide and the acetylenic hydrocarbon are heated to boiling for 24 hours, a slight excess of ethyl orthoformate is then added, and the heating continued for a further 24 hours; the yield of the acetal thus obtained amounts to 75 per cent. of the theoretical. *Amylpropiolaldehyde* ortho*diethylic ether*,

$$C_5H_{11}\cdot C:C\cdot CH(OEt)_2,$$

boils at 110° under 11 mm. pressure, has n_D 1·438 at 15°, and a sp. gr. 0·881 at 15°/0°. *Hexylpropiolaldehyde* ortho*diethylic ether*,

$$C_6H_{13}\cdot C:C\cdot CH(OEt)_2,$$

boils at 127° under 12 mm. pressure, has n_D 1·441 at 12°, and a sp. gr. 0·879 at 12°/0°. Phenylpropiolaldehyde orthodiethylic ether boils at 144—145° under 14 mm. pressure, has n_D 1·521 at 14°, and sp. gr. 0·995 at 14°/0° (compare Claisen, Abstr., 1897, i, 188).

The aldehydes obtained by hydrolysis of the first and third compounds have already been described (compare Abstr., 1901, i, 250, and Claisen, Abstr., 1898, i, 421, 422). *Hexylpropiolaldehyde*,

$$C_6H_{13}\cdot C:C\cdot CHO,$$

distils at 90—92° under 13 mm. pressure and has a sp. gr. 0·909 at 0°. The aldehydes combine with sodium hydrogen sulphite; their semicarbazones melt respectively at 90° (amyl), 78—79° (hexyl), and 137—138° (phenyl); by the action of hydroxylamine hydrochloride in the presence of sodium acetate, the oximes are not formed, but their corresponding *iso*oxazoles (compare this vol., i, 95); 5-*amyl*iso*oxazole*, $O<\begin{matrix}N{=\!=\!=}CH\\ C(C_5H_{11}){:}CH\end{matrix}$, boils at 87—87·5° under 14 mm. pressure and has a sp. gr. 0·954 at 0°/0°; 5-*hexyl*iso*oxazole*, $O<\begin{matrix}N{=\!=\!=}CH\\ C(C_6H_{13}){:}CH\end{matrix}$, boils at 103—104° under 15 mm. pressure and has a sp. gr. 0·943 at 0°/0°; 5-phenyl*iso*oxazole melts at 18—22°, boils at 131° under 17 mm. pressure and at 254—256° (corr.) under normal pressure. M. A. W.

Chloralacetonechloroform. F. HOFMANN-LA ROCHE & Co. (D.R.-P. 151188).—Acetonechloroform and chloral hydrate are heated together for ½ hour at 75—80° and the product dissolved in benzene.

Chloralacetonechloroform, $CCl_3 \cdot CMe_2 \cdot O \cdot CH(OH) \cdot CCl_3$, separates in asbestos-like needles, melts at 65°, and has a faint odour and taste of camphor. It sublimes when cautiously heated. Sulphuric acid hydrolyses it in the cold to chloral and acetonechloroform, potassium permanganate is only reduced on warming. The compound possesses hypnotic and local anæsthetic properties. C. H. D.

Mutual Transformation of the Two Stereoisomeric Penta-acetates of Dextrose. Coenraad L. Jungius (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 779—783. Compare Abstr., 1903, i, 733).—The particular penta-acetate formed by the action of acetic anhydride on dextrose depends on the catalyser used; with dry sodium acetate, the β-form, melting at 134°, is produced (Franchimont, Herzfield), whilst with zinc chloride, the α-form, melting at 112°, is obtained (Erwin and Königs). The β- is readily converted into the α-isomeride by boiling its solution in acetic anhydride with a little zinc chloride, and the author has made a closer study of this transformation, which he finds to be caused by an intramolecular migration at the terminal asymmetric carbon atom. The transformation is not due to the addition and subsequent elimination of a molecule of the solvent, since Lobry de Bruyn has shown that by simple melting of the β-isomeride with dry zinc chloride, the α-isomeride is formed. The author has succeeded in effecting the same transformation in a chloroform solution containing sulphur trioxide.

As in the case of the two methyl glucosides, the final condition in the transformation results in a state of equilibrium. The optical activity of a solution of the β-form in acetic anhydride, together with zinc chloride, gradually increased with measurable velocity to a constant value, which was also attained in a similar manner when the α-form was employed. It is calculated that in the condition of equilibrium there exists 88 per cent. of the α- and 12 per cent. of the β-compound. The action is unimolecular; the velocity constant is 0·0095 at 35° with a concentration of 2 per cent. of zinc chloride, whilst at 45° the constant is 0·028; with 1 per cent. solutions of zinc chloride at 45°, the constant is 0·0135.

Tanret's third penta-acetate of dextrose is shown not to exist; it is simply a mixture of the α- and β-forms. If it were really a third isomeride, it might be obtained free from the others by crystallisation, and should present a definite melting point. If a mixture of the α- and β-forms is made in such proportion that the $[\alpha]_D$ is 60°, the product shows the same melting point as that given by Tanret for the third isomeride, namely, 91—94°. A solution saturated with both isomerides and a solution saturated with Tanret's product contain the same amount of penta-acetate, the solvent being 50 per cent. alcohol.

The two stereoisomeric methyl glucosides may be converted into the corresponding penta-acetates, and the latter into the former (Fischer and Armstrong, Abstr., 1901, i, 671). The α-glucoside corresponds with the α-penta-acetate and the β-glucoside with the β-penta-acetate.

The mutual transformation of the methylglucosides (Jungius, Abstr., 1903, i, 733) and the penta-acetates described conditions the multi-

rotation of those substances (compare Armstrong, Trans., 1903, 83, 1305). A. McK.

Constitution of Cellulose. Charles F. Cross and Edward J. Bevan (*Zeit. Farb. Text.-Ind.*, 1904, 3, 197—199).—A theoretical paper unsuitable for abstraction (compare Green, *ibid.*, 97). W. A. D.

Isolation of Betaine from the Waste Liquors from the Desaccharification of Molasses by means of Strontia. Karl Andrlík (*Zeit. Zuckerind. Böhm.*, 1904, 28, 404—406).—After separating the amino-acids from these waste liquors by means of phosphoric acid and alcohol (see Abstr., 1903, i, 797), the alcoholic solution is treated further with syrupy phosphoric acid, by which means crystalline betaine phosphate is obtained. This phosphate is decomposed by means of milk of lime, the solution freed from lime by carbon dioxide, and the filtrate evaporated on the water-bath ; on cooling, it solidifies to a crystalline mass of betaine, which is purified by crystallisation from 96 per cent. alcohol. In this way, a yield of pure betaine equal to 12 per cent. of the dry matter of the original waste liquors may be obtained. T. H. P.

Synthesis of Polypeptides. Emil Fischer (*Ber.*, 1904, 37, 2486—2511. Compare Abstr., 1903, i, 465 and 799).—By making use of the method previously described, namely, the condensation of amino-acids with halogen-substituted acid chlorides, a large number of polypeptides of all classes have been prepared. i-*Glycylalanine*, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H$, prepared by heating chloroacetylalanine with ammonia, melts and decomposes at 227° (corr.) and forms a carbethoxy-derivative identical with that previously described. The intermediate *chloroacetylalanine* crystallises in colourless, four-sided, oblique plates melting at 125—127° (corr.). α-*Bromo*iso*hexoylleucine*, $CHMe_2{\cdot}CH_2{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CHMe_2$, prepared by the interaction of leucine and bromo*iso*hexoyl chloride, crystallises in oblique, four-sided plates, which melt to a clear liquid at 188—189° (corr.) and on heating with ammonia form leucyl-leucine (*loc. cit.*). *Chloroacetyl*-l-*tyrosine* crystallises in prisms melting at 155—156° (corr.) and shows Millon's reaction. The corresponding ester, prepared by the action of chloroacetyl chloride on tyrosine ethyl ester, crystallises in needles melting at 87—88° (corr.). Both compounds, when heated at 100° with aqueous ammonia, form *glycyl*-l-*tyrosine*,

$$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}C_6H_4{\cdot}OH,$$

which sinters at 125° and melts at 165°. Trypsin at 36° hydrolyses it, separating tyrosine. The *ethyl* ester melting at 245° (corr.) has been obtained crystalline. α-*Bromo*iso*hexoyl*-l-*tyrosine*, which can be prepared either from tyrosine itself or from its ethyl ester, crystallises from water in globular aggregates of needles and melts at 139—140° (corr.). It and the following compound are possibly mixtures of two stereoisomerides. On heating with ammonia, *leucyl*-l-*tyrosine* is formed, which shows Millon's reaction and dissolves copper oxide with a deep blue coloration, but has as yet only been obtained in an amorphous condition.

Leucyltyrosine anhydride, $C_4H_9 \cdot CH <\substack{CO \cdot NH \\ NH \cdot CO}> CH \cdot CH_2 \cdot C_6H_4 \cdot OH$, which is obtained as a by-product and is best prepared by heating the oily ethyl ester from α-bromo*iso*hexoyltyrosine with alcoholic ammonia, crystallises in slender needles and melts and decomposes at 310° (corr.).

The preparation of diglycylglycine (*loc. cit.*, 799) is improved by preparing chloroacetylglycylglycine directly from glycylglycine hydrochloride and chloroacetyl chloride and subjecting this compound to the action of ammonia in the cold instead of at 100°.

Chloroacetyldiglycylglycine, which melts and decomposes at 224° (corr.), yields, on heating with aqueous ammonia at 100°, the tetrapeptide, *triglycylglycine*,

$$NH_2 \cdot CH_2 \cdot CO \cdot [NH \cdot CH_2 \cdot CO]_2 \cdot NH \cdot CH_2 \cdot CO_2H;$$

this colours at 220° and becomes quite dark at 270° without melting; it shows a biuret coloration in alkaline solution and is soluble in about 4 parts of hot water. The hydrochloride of the ethyl ester melts at 212—214° (Curtius, Abstr., 1902, i, 844, gives 192—193°) and the benzoyl derivative at 235° (Curtius, *loc. cit.*). *α-Bromo*iso*hexoyl-leucylglycylglycine*, prepared by the interaction of leucylglycylglycine and α-bromo*iso*hexoyl chloride, sinters at 152° and melts at 161—162° (corr.); when heated with ammonia, i-*dileucylglycylglycine*,

$$NH_2 \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot [CO \cdot NH \cdot CH_2]_2 \cdot CO_2H,$$

is formed. This crystallises in microscopic needles aggregated in bunches and melts about 250°.

Chloroacetyltriglycylglycine becomes yellow at 230° and melts and decomposes at 256° (corr.). On heating with ammonia, the pentapeptide *tetraglycylglycine*, $NH_2 \cdot CH_2 \cdot CO \cdot [NH \cdot CH_2 \cdot CO]_3 \cdot NH \cdot CH_2 \cdot CO_2H$, is formed; this is sparingly soluble in water; on heating, it becomes coloured at 246° (corr.) and decomposes at higher temperatures.

αβ-Dibromopropionyl chloride (Moureu, Abstr., 1903, i, 312) is conveniently prepared by the interaction of αβ-dibromopropionic acid with an equal weight of phosphorous pentachloride; it boils at 71—73° under 12 mm. pressure and reacts readily with the peptides.

αβ-Dibromopropionylglycine crystallises in needles, melting at 147—148° (corr.) and decomposing at 170°. *αβ-Dibromopropionylglycylglycine* forms microscopic, obliquely cut prisms melting at 184° (corr.). The *ethyl* ester prepared from glycylglycine ester crystallises in prisms, which sinter at 145° and melt at 151—152° (corr.). *Bromoacrylglycylglycine*, $C_2H_2Br \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, prepared by the action of cold sodium hydroxide on the preceding compound, crystallises in prisms melting at 202° (corr.). The possibility of the formation of stereoisomerides by these syntheses is also discussed. E. F. A.

Evidence for the Possibility of Resolving an Optically Active Compound without actually Resolving it and without the Aid of Optically Active Substances. Ernst Mohr (*Ber.*, 1904, 37, 2702—2704).—E. Fischer has indicated (preceding abstract) that, in the preparation of dipeptides of the type

$$NH_2 \cdot CHR \cdot CO \cdot NH \cdot CHR \cdot CO_2H,$$

a mixture of two stereoisomeric racemic products may be obtained in different amounts, starting with inactive material.

Since, theoretically, in the general reaction $\overset{*}{C}HXY{\cdot}COCl + NH_2{\cdot}\overset{*}{C}HUV = HCl + \overset{*}{C}HXY{\cdot}CO{\cdot}NH{\cdot}\overset{*}{C}HUV$ (where the asymmetric carbon atoms are represented by *), a mixture of two stereoisomeric racemic acid amides may be formed, reactions of this nature may be of use in settling whether a given acid chloride or amine is racemic or not.

The author finds that the product from the reaction

$$C_6H_5{\cdot}CH_2{\cdot}CHEt{\cdot}COCl + NH_2{\cdot}CHMePh = HCl + C_6H_5{\cdot}CH_2{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}CHMePh$$

is a mixture melting at 60—80°, which, by systematic crystallisation from light petroleum, may be separated into two isomeric substances. The more sparingly soluble constituent separates in slender, white needles, softens at 109°, and melts at 112°; the isomeride forms silky needles, softens at 75°, and melts at 85—87°. The latter is present in the mixture in larger quantity than the former.

In accordance with theory, the compounds

$$CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CHMePh$$

(m. p. 89°) and $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$ (m. p. 85°) exist in one modification only. A. McK.

Constitution of Purpuric Acid and Murexide. RICHARD MÖHLAU (*Ber.*, 1904, 37, 2686—2691).—Piloty points out (*Annalen*, 1904, 333, Heft 1) that Matignon's formula for purpuric acid,

$$CO{<}{\begin{smallmatrix}NH{\cdot}CO\\NH{\cdot}CO\end{smallmatrix}}{>}C\overset{NH}{\triangle}C{<}{\begin{smallmatrix}CO{\cdot}NH\\CO{\cdot}NH\end{smallmatrix}}{>}CO,$$

which represents this acid as an imide of alloxantin, is in accordance neither with its instability nor with the intense coloration of its salts. The formula $CO{<}{\begin{smallmatrix}NH{\cdot}CO\\NH{\cdot}CO\end{smallmatrix}}{>}C{:}N{\cdot}CH{<}{\begin{smallmatrix}CO{\cdot}NH\\CO{\cdot}NH\end{smallmatrix}}{>}CO$ is more probably correct, since murexide is decomposed by boiling its aqueous solution into alloxan and uramil, a little alloxantin being also formed. The author further gives evidence for the existence of purpuric acid in the free state, and shows that the acid itself splits up into alloxan and uramil.

Dibarbiturylmethylamine, prepared by boiling an aqueous solution of alloxantin (or dialuric acid) with methylamine hydrochloride, separates from water in transparent, rhombic crystals, which decompose at 240°. By oxidation of this compound, however, it was not found possible to prepare an *N*-substituted murexide.

Piloty's views as to the constitution of murexide are discussed. The author considers murexide to be a ketoimide having the constitution

$$CO{<}{\begin{smallmatrix}NH{\cdot}CO\\NH{\cdot}CO\end{smallmatrix}}{>}C{:}N{\cdot}C(NH_4){<}{\begin{smallmatrix}CO{\cdot}NH\\CO{\cdot}NH\end{smallmatrix}}{>}CO \text{ or}$$

$$CO{<}{\begin{smallmatrix}NH{\cdot}CO\\NH{\cdot}CO\end{smallmatrix}}{>}C{:}N{\cdot}C{\lessdot}{\begin{smallmatrix}CO\text{———}NH\\C(ONH_4){\cdot}NH\end{smallmatrix}}{>}CO.$$

A. McK.

Preparation of Hydrogen Cyanide. Hermann Charles Woltereck (D.R.-P. 151130).—Kuhlmann's synthesis of hydrogen cyanide (1841) by passing ammonia and a volatile hydrocarbon over a heated catalytic substance may be employed technically if care is taken to dry the gases thoroughly and to ensure the presence of free hydrogen. The temperature required is higher the more complex the carbon compound employed. A mixture of 1 part of ammonia and 2 parts of water-gas (carbon monoxide and hydrogen) may be used with advantage. The mixed dry gases are passed over platinised pumice heated to bright redness, and the hydrogen cyanide formed is absorbed in water or solutions of alkali hydroxides. C. H. D.

[Preparation of Cyanogen Compounds.] Hermann Mehner (D.R.-P. 151644).—The preparation of cyanides from alkalis, carbon, and atmospheric nitrogen in a furnace offers great difficulties. An improved arrangement is described, in which a cupola furnace containing coal or coke is used, air being forced through the burning mass. Water-glass or an alkaline or alkaline earthy slag is added at the top of the furnace, and, becoming strongly heated, descends to the lower part, which acts as a Siemens' producer and contains a reducing atmosphere. Here cyanogen compounds are formed, and escape, mixed with carbon monoxide and some nitrogen, through an outlet near the base of the furnace. The products of combustion in the upper (oxidising) portion escape at the top. The hot slag is returned to the furnace, loss of alkali being made good by the addition of sodium carbonate. Metallic iron, formed by reduction of the ash of the coke, accumulates in the slag and greatly facilitates the reaction (compare Täuber, Abstr., 1901, ii, 107; 1903, i, 328). C. H. D.

A Constituent of Gas Purification Residues: Iron Carbonylferrocyanide. Max Stoecker (*Chem. Centr.*, 1904, i, 1406; from *J. f. Gasbel.*, 47, 338—342. Compare Abstr., 1904, i, 147).—The residues obtained in the purification of coal gas contain only an extremely small quantity of iron carbonylferrocyanide, and attempts to isolate this compound failed. Large quantities have been prepared, however, from the violet filtrate obtained after precipitating the potassium ferrocyanide with ferric chloride. The iron carbonylferrocyanide was converted into the potassium salt by four different methods. Potassium carbonylferrocyanide, $K_3FeCO(CN)_5$, forms small, faintly yellow to colourless crystals which contain varying amounts of water of crystallisation. Iron carbonylferrocyanide, $Fe'''Fe''CO(CN)_5$, prepared by the action of an excess of ferric chloride on the corresponding potassium compound, resembles indigo in appearance and contains about 4 per cent. of water of crystallisation. The usual methods of estimating the quantity of Prussian blue in gas residues, such as those of Knublauch, Drehschmidt, &c., give results which include the amount of the violet carbonyl compound which is also present. Owing to the very small proportion of the latter, however, and the ease with which it is converted into Prussian blue, the error is of no practical importance. The carbonyl compounds are almost entirely converted into Prussian blue in the purification process itself;

in a residue containing 10 per cent. of Prussian blue, there would only be about 0·1 per cent. of the pure violet compound.

Iron carbonylferrocyanide is prepared from the last mother liquor obtained in the preparation of potassium ferrocyanide. The liquor, which contains potassium carbonylferrocyanide together with a considerable quantity of potassium ferrocyanide and other salts, is precipitated with ferric chloride, the precipitate decomposed by alkali by Lindemann's method, the ferric hydroxide removed, the filtrate evaporated to dryness, and the residue melted with powdered iron.

E. W. W.

Dibenzoyldiazomethane. HEINRICH WIELAND and SIEGFRIED BLOCH (*Ber.*, 1904, 37, 2524—2528. Compare this vol., i, 596).—*Dibenzoyldiazomethane*, prepared from dibenzoylmethane in cold ethereal solution by the action of nitrous fumes and isolated under special precautions, crystallises from 96 per cent. alcohol in yellow, rhombic plates melting and decomposing violently at 114°; it shows all the reactions of aliphatic diazo-compounds. *Anilinodibenzoylmethane*, $CHBz_2{\cdot}NHPh$, prepared from it by heating with aniline, crystallises in colourless needles melting at 168—169°. E. F. A.

Alkyl Derivatives of Thallium. RICHARD J. MEYER and ALFRED BERTHEIM (*Ber.*, 1904, 37, 2051—2062).—A new method is described of preparing dialkylthallium compounds from thallium chloride by means of magnesium alkyl haloids.

Thalliumdimethyl bromide, $TlMe_2Br$, crystallises in white, silvery flakes and decomposes with liberation of gas above 275°.

Thalliumdimethyl iodide, $TlMe_2I$, precipitated by potassium iodide from the mother liquors of the bromide, crystallises from dilute ammonia in silver-white flakes and decomposes at 264—266°.

Thalliumdimethylthiol, $TlMe_2{\cdot}SH$, decomposes with incandescence when heated or when dropped into fuming nitric acid.

Thalliumdimethyl chloride, $TlMe_2Cl$, separates in glistening, white, shimmering scales and decomposes above 280°.

Thalliumdiethyl chloride, $TlEt_2Cl$, resembles the preceding compound, but is less soluble and decomposes at 205—206°. The iodide, $TlEt_2I$, crystallises from pyridine and decomposes at 185—187°. The *bromide*, $TlEt_2Br$, decomposes above 270°. The *thiol*, $TlEt_2{\cdot}SH$, resembles the methyl derivative. The *hydroxide*, $TlEt_2{\cdot}OH$, prepared by the action of silver oxide on the iodide, dissolves readily in water and alcohol, is a strong alkali, rapidly absorbs carbon dioxide, and precipitates metallic hydroxides from their salts; unlike its salts, it melts at 127—128° and decomposes at a higher temperature. The *carbonate*, $(TlEt_2)_2CO_3$, crystallises from water in glistening needles, decomposes at 204°, and has all the properties that Hartwig (Abstr., 1875, 1002) ascribed to the base. The *hydrogen carbonate*, $TlEt_2{\cdot}HCO_3$, is precipitated as a white, feebly alkaline, crystalline powder when carbon dioxide is passed into a solution of the carbonate and alcohol then added.

Thalliumdipropyl chloride, $TlPr_2Cl$, crystallises from dilute ammonia in silvery flakes and decomposes at 198—202°. The *iodide* decom-

poses at 183—185°. The *nitrate* is sparingly soluble and crystallises exceptionally well. The *thiol* resembles those just described. The *hydroxide* was obtained only as an oil.

Thalliumdiphenyl bromide, $TlPh_2Br$, crystallises from alcoholic ammonia or from pyridine in minute, white needles and decomposes at 270°.

In all these compounds, the tervalent character of the thallium is very strongly marked. T. M. L.

Action of Dilute Nitric Acid on Haloid Compounds. II. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 537—539).—The action of dilute nitric acid on bromo-*o*-xylene yields:

(1) 5-*Bromo-ω-nitro-o-xylene*, $C_6H_3MeBr{\cdot}CH_2{\cdot}NO_2$, which melts at 65°; its salts, when mixed with ferric chloride and ether, give the reaction for nitro-compounds.

(2) 5-*Bromo-o-toluic acid*, $C_6H_3MeBr{\cdot}CO_2H$, which may also be obtained by oxidising the compound (1) by means of potassium permanganate and which melts at 175°.

(3) A liquid nitro-compound.

With bromo-*p*-xylene, dilute nitric acid gives a liquid and a solid nitro-compound, the latter melting at 198—200°. T. H. P.

Nitration of *p*-Tolylnitromethane [ω-Nitro-*p*-xylene]. MICHAEL I. KONOWALOFF and SENTSCHIKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 462—465).—When a hydrogen atom in the benzene nucleus is replaced by the residue, ${\cdot}CH_2{\cdot}NO_2$, the latter influences a nitro-group entering the nucleus in the same way as do the groups NO_2, CHO, CO_2H; that is, the nitro-group will enter in the meta-position to the ${\cdot}CH_2{\cdot}NO_2$, if that position is unoccupied, or in the ortho-position if the meta-position is occupied, and the nitration is carried out in the cold with nitric acid of sp. gr. 1·48. T. H. P.

Iodoso-, Iodoxy-, and Iodinium-compounds of 4-Iodo-1-methyl-3-ethylbenzene. CONRAD WILLGERODT and LOUIS BRANDT (*J. pr. Chem.*, 1904, [ii], 69, 433—448).—4-*Amino*-1-*methyl*-3-*ethylbenzene*, obtained by heating ethyl alcohol and *p*-toluidine with zinc chloride at 280°, distils at 218—220°. The *sulphate*,

$$(C_6H_3MeEt{\cdot}NH_2)_2,H_2SO_4,$$

crystallises in large leaflets and melts at 241°. When the base is diazotised and warmed with absolute alcohol, a red *oil* is obtained. This boils at 160°, and, when oxidised successively with nitric acid and with potassium permanganate in alkaline solution, yields *iso*phthalic acid.

The action of potassium iodide on diazotised 4-amino-1-methyl-3-ethylbenzene leads to the formation of 4-*iodo*-1-*methyl*-3-*ethylbenzene*, which crystallises in glistening leaflets, melts at 34°, and boils at 222—225°. When acted on by chlorine in glacial acetic acid solution, it yields the *iodochloride*, $C_6H_3MeEt{\cdot}ICl_2$, which crystallises in long needles and melts at 108°.

4-*Iodoso*-1-*methyl*-3-*ethylbenzene*, $C_6H_3MeEt{\cdot}IO$, is amorphous and explodes at 209°. The *iododiacetate* crystallises in clear, transparent

prisms. The basic *sulphate*, $SO_4[I(OH)\cdot C_6H_3MeEt]_2$, crystallises in prisms.

4-*Iodoxy*-1-*methyl* 3-*ethylbenzene*, $C_6H_3MeEt\cdot IO_2$, prepared by the action of sodium hypochlorite on the iodoso-compound, crystallises in white leaflets and explodes at 229°.

Di-1-*methyl*-3-*ethylphenyliodinium hydroxide*, $I(C_6H_3MeEt)_2\cdot OH$, prepared from the iodoso- and iodoxy-compounds, is obtained as a strongly alkaline aqueous solution. The *chloride* melts at 120°; the *bromide* melts at 162°; the *iodide* is a yellow, amorphous substance; the *mercurichloride* crystallises in transparent plates and melts at 197°; the orange-coloured *platinichloride* melts and decomposes at 166°.

The action of cold concentrated sulphuric acid on 4-iodoso-1-methyl-3-ethylbenzene leads to the formation of 1-*methyl*-3-*ethylphenyl*-(?)-*iodo*-1′-*methyl*-3′-*ethylphenyl*-4-*iodinium hydroxide*,

$$C_6H_3MeEt\cdot I(C_6H_2IMeEt)\cdot OH$$

(Hartmann and Meyer, Abstr., 1894, i, 242), which is obtained in a strongly alkaline aqueous solution. The *chloride* is a white, amorphous powder and melts and decomposes at 157°; the *bromide* is amorphous and melts at 151°; the *iodide* is obtained as a yellow, amorphous precipitate and melts and decomposes at 145°; the *platinichloride* is a yellow powder and melts at 173°.

o-*Tolyl*-1-*methyl*-3-*ethylphenyl*-4-*iodinium hydroxide*,

$$C_7H_7\cdot I(C_9H_{11})\cdot OH,$$

is obtained from *o*-iodoxytoluene and 4-iodoso-1-methyl-3-ethylbenzene as an alkaline solution in water. The *chloride* melts at 177°; the *bromide* is obtained as a white, amorphous precipitate and melts at 175°; the *iodide* is a yellow, amorphous powder which melts at 168°; the *platinichloride* is orange-coloured and melts at 176°; the *dichromate* is obtained as a red precipitate.

1-*Methyl*-3-*ethylphenyldichloroethyliodinium chloride*,

$$C_2H_3Cl_2\cdot I(C_9H_{11})\cdot Cl,$$

prepared by the action of silver chloride and silver acetylide on methylethylphenyl iodochloride (Abstr., 1895, i, 635), is a white, amorphous powder, which melts and decomposes at 171°; the *bromide* is a white, amorphous powder and melts and decomposes at 150°; the yellow, amorphous *iodide* melts at 96°; the orange-coloured *platinichloride* melts at 132°; the *mercurichloride* melts at 121°; the *dichromate* forms a yellow, flocculent precipitate. G. Y.

Triphenylmethyl. IX. Moses Gomberg and L. H. Cone (*Ber.*, 1904, **37**, 2033—2051. Compare Abstr., 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244).—The substance was prepared by the action of zinc on the chloride in a special form of apparatus, in which the whole operation of preparing the crystalline compound was effected in an atmosphere of carbon dioxide. The purified compound is quite insoluble in light petroleum, ethyl chloroacetate, and ethyl chlorocarbonate, and only sparingly soluble in chlorobenzene, benzyl chloride, and hot ethyl and methyl alcohols. It is moderately soluble in carbon tetrachloride and in toluene (from which magnificent crystals separate containing toluene), more so on heating or in ethyl iodide and ethylene bromide, and very readily in hot or cold chloroform and

carbon disulphide. The purest material melted at 145—147°, but not sharply. Distillation under reduced pressure gave triphenylmethane. Molecular weight determinations in an atmosphere of nitrogen gave, as a mean of 12 series of observations in benzene, naphthalene, nitrobenzene, dimethylaniline, *p*-bromotoluene, and phenol, the mean value M = 477, whilst $(C_6H_5)_3C$ requires M = 243, so that the substance is clearly dimolecular. This conclusion was confirmed by the observation that the depression of the freezing point of a solution of the chloride in nitrobenzene gradually decreased from 0·567 to 0·311, and from 1·197 to 0·647 in two series of experiments in which the chloride was converted into triphenylmethyl by the action of silver. The figures quoted correspond with a rise of molecular weight in the ratios 279 to 509 and 278 to 514.

Walden's observation that solutions of triphenylmethyl in sulphur dioxide have a marked conductivity was confirmed with freshly prepared and highly purified material. The molecular conductivity (M = 486) rose from $\mu = 16·48$ when $v = 24$ to $\mu = 39·6$ when $\mu = 2138$, and similar values were obtained in three other series of observations.

Triphenylmethyl is shown by this series of observations to be a dimolecular compound, but is not identical with hexaphenylethane. The nature of the isomerism is still somewhat obscure, but the author maintains the view that the compound is essentially a derivative of tervalent carbon, CPh_3–, although in solution there is a tendency to form a loose bimolecular compound, which may be compared to the loose polymerides of water, nitriles, and organic acids. T. M. L.

Bistriphenylmethyl and Hexaphenylethane. Daniel Vorländer (*Ber.*, 1904, **37**, 2397. Compare Gomberg, this vol., i, 489).—Bistriphenylmethyl and hexaphenylethane form an example of additive isomerism. The properties of these two substances are expressed by the formulæ $(CPh_3)(CPh_3)$ for bistriphenylmethyl and $CPh_3·CPh_3$ for hexaphenylethane. G. Y.

***s*-9 : 10-Diphenylanthracene and 9 : 10-Diphenyldihydroanthracene.** Albin Haller and Alfred Guyot (*Compt. rend.*, 1904, **138**, 1251—1254. Compare this vol., i, 83, 314, 346).—Phenyloxanthranol, $C_6H_9{<}{\overset{CPh(OH)}{\underset{CO}{}}}{>}C_6H_4$, melting at 207°, is obtained when an ethereal solution of magnesium phenyl bromide is slowly added to a suspension of anthraquinone in anhydrous ether. By further action of the magnesium compound on phenyloxanthranol, 9 : 10-dihydroxy-9 : 10-diphenyldihydroanthracene,

$$C_6H_4{<}{\substack{CPh(OH)\\CPh(OH)}}{>}C_6H_4,$$

is obtained. The *monomethyl ether* forms colourless crystals melting at 274°. The diol, or ether, when treated with alcoholic hydrogen chloride in boiling solution in glacial acetic acid, gives the *dichloride*,

$$C_6H_9{<}{\substack{CPhCl\\CPhCl}}{>}C_6H_4,$$

melting at 178°. The chloride acts as an energetic oxidising agent, and

by loss of chlorine is converted into 9 : 10-*diphenylanthracene*,

$$C_6H_4<\overset{CPh}{\underset{CPh}{|}}>C_6H_4.$$

The hydrocarbon is most readily obtained by treatment of the dichloride with zinc or potassium iodide in acetic acid solution; it separates from carbon disulphide in yellow crystals melting at 240°, and in most solvents it exhibits fluorescence.

9 : 10 *Diphenyldihydroanthracene*, $C_6H_4<\overset{CHPh}{\underset{CHPh}{}}>C_6H_4$, obtained by the prolonged action of sodium amalgam on 9 : 10-diphenylanthracene suspended in alcohol, dissolves readily in toluene and is precipitated by alcohol in slender needles melting at 218°. On heating, it loses hydrogen; its solutions do not fluoresce. H. M. D.

Syntheses in the Anthracene Series. II. 9:9:10-Triphenyldihydroanthracene and Derivatives. Albin Haller and Alfred Guyot (*Compt. rend.*, 1904, 139, 9—13. Compare Abstr., 1901, i, 350; 1903, i, 200, 348; this vol., i, 83, 314, 346).—10-*Hydroxy-9 : 9 : 10-triphenyldihydroanthracene*, $C_6H_4<\overset{CPh_2}{\underset{CPh(OH)}{}}>C_6H_4$, obtained quantitatively by means of the Grignard synthesis from diphenylanthrone and magnesium phenyl bromide, forms colourless, voluminous crystals containing ether (1 mol.), which it loses at 120°, melts at 200°, resembles triphenylcarbinol in giving an orange-red coloration with sulphuric acid, in forming condensation products with phenol (compare Baeyer and Villiger, Abstr., 1902, i, 769) and with aniline (compare Ullmann and Münzhuber, Abstr., 1903, i, 245), and in being readily etherified by boiling with alcohol and a few drops of hydrochloric acid; the *methyl ether* forms white, pearly plates melting at 218°, and the *ethyl ether* forms white needles melting at about 250°. 9 : 9 : 10-*Triphenyldihydroanthracene*, $C_6H_4<\overset{CPh_2}{\underset{CHPh}{}}>C_6H_4$, obtained by reducing the hydroxy-compound by means of zinc and acetic acid, forms white crystals melting at about 220°, and is sparingly soluble in the ordinary solvents. A second synthesis of this hydrocarbon is effected by means of the Grignard reaction from *methyl triphenylmethane-o-carboxylate*, which is prepared by the action of methyl sulphate on an alkaline solution of triphenyl methane-*o*-carboxylic acid, forms white prisms melting at 98°, and condenses with magnesium phenyl bromide to form the compound $OMe\cdot CPh_2\cdot C_6H_4\cdot CHPh_2$, which melts at 215° and readily loses a mol. of methyl alcohol on treatment with concentrated sulphuric or hydrochloric acid to form 9 : 9 : 10-triphenyldihydroanthracene.

Attempts to effect a further synthesis of this hydrocarbon from methyl phthalate or methyl benzoylbenzoate and magnesium phenyl bromide were unsuccessful. M. A. W.

Direct Reduction of the Homologues of Aniline. Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1904, 138, 1257—1259).—The authors have previously shown (this vol., i, 305) that, under the influence of hot, finely-divided nickel, aniline is reduced

to *cyclo*hexylamine with secondary formation of di*cyclo*hexylamine and *cyclo*hexylaniline. The homologues of aniline have now been investigated. Methyl- and ethyl-anilines give respectively cyclo*hexylmethylamine*, $C_6H_{11}\cdot NHMe$, boiling at 145°, and cyclo*hexylethylamine* boiling at 164° (corr.), having a sp. gr. 0·868 at 0°/0°. The odour of these liquids strongly resembles that of methyl- and ethyl-amines. With phenylcarbimide, the ethyl compound yields *phenyl*cyclo*hexylethylcarbamide*, $NHPh\cdot CO\cdot NEt\cdot C_6H_{11}$, which crystallises in colourless, rhombic laminæ and melts at 125° (corr.); the corresponding *thiocarbamide* melts at 126°. cyclo*Hexyldimethylamine*, boiling at 165° (corr.) and having a sp. gr. 0·876 at 0°/0°, and the corresponding *diethyl* compound, boiling at 193° (corr.) and having a sp. gr. 0·872 at 0°/0°, are similarly formed from dimethyl- and diethyl-aniline. The secondary actions observed in the case of aniline are not met with in the reduction of the above homologues. On the other hand, *m*-toluidine behaves quite similarly to aniline and gives rise to three products, one of which is 1 : 3-*methyl*cyclo*hexylamine*, which boils at 150°, and the other two appear to be *dimethyl*cyclo*hexylamine*, boiling at 145° under 20 mm. pressure, and *methyl*cyclo*hexylaniline*, boiling at 175° under 20 mm. pressure. H. M. D.

Conditions of the Interaction between Aniline Vapour and Aluminium Chlorate Solution. DMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 483—485).—Filter paper soaked in aluminium chlorate solution and left in the laboratory in presence of aniline vapour gradually assumes an intense blue colour, which slowly changes to a dirty green. This phenomenon is due to oxidation of the aniline, the final product of which is known as nigraniline, which is an extremely stable dye. The blue colour obtained is that of an intermediate, basic, oxidation product which, in the form of salts of a green colour, is known as emeraldine. Glass smeared with nitric acid also becomes coloured in presence of aniline vapour, the final product being emeraldine. T. H. P.

Iodine Derivatives of *m*-Nitroaniline. P. BRENANS (*Compt. rend.*, 1904, **138**, 1503—1505; **139**, 63—65. Compare Abstr., 1901, i, 322, 643; 1902, i, 280, 673; 1903, i, 336; this vol., i, 157).—By the action of iodine chloride on *m*-nitroaniline in acetic acid solution, three iodine derivatives were obtained: I. 6-*iodo*-3-*nitroaniline* crystallises from alcohol in yellow needles melting at 160° (corr.), is soluble in all ordinary organic solvents except light petroleum, and on diazotising and boiling with alcohol yields 1-iodo-4-nitrobenzene melting at 171·5° and identical with the compound obtained by substituting iodine for the NH_2 group in *p*-nitroaniline. II. 2 : 5-*Di-iodo*-3-*nitroaniline* crystallises from a mixture of chloroform and light petroleum in large, yellow prisms melting at 125° (corr.), is very soluble in the ordinary solvents with the exception of light petroleum, and, on diazotising with amyl nitrite and subsequent boiling, yields 1 : 3-*di-iodo*-2-*nitrobenzene*, which crystallises from a mixture of chloroform and light petroleum in large prisms melting at 114° (corr.), soluble in all the ordinary solvents except light petroleum, and is reduced by ferrous sulphate

and ammonia to 1:6-*di-iodoaniline*, which crystallises in colourless needles melting at 122° (corr.), is soluble in the ordinary solvents, forms a *diacetyl* derivative crystallising in colourless needles melting at 147° (corr.), and on diazotising and boiling with water yields 1 : 6-di-iodophenol, melting at 68° and identical with the compound prepared by Schaal (compare Abstr., 1883, 1109). III. 2 : 6-Di-iodo-3-nitroaniline, identical with the compound prepared by Michael and Norton (compare Abstr., 1878, 406), crystallises in orange-yellow needles melting at 149° (corr.), soluble in all the ordinary organic solvents except light petroleum, and on diazotising and boiling with alcohol yields 2 : 4-*di-iodonitrobenzene*, which forms yellow crystals, melts at 101°, resembles the preceding compound in solubility, and is reduced by stannous chloride to 2 : 4-di-iodoaniline, identical with Michael's compound (compare *loc. cit.*), and forming a *di-acetyl* derivative which crystallises in thin, colourless needles from alcohol, melts at 93°, and is very soluble in alcohol and acetic acid. The identity of the di-iodoaniline was further confirmed by converting it by the ordinary processes into the corresponding phenol. The compound thus obtained melted at 72° and was identical with Schaal's 2 : 4-di-iodophenol (Abstr., 1883, 1109).

Koerner has described a 2 : 4-di-iodonitrobenzene melting at 168·4°, and obtained by heating 1 : 3-di-iodobenzene with fuming nitric acid (Abstr., 1876, i, 222); the author has repeated the experiment and finds that the compound melting at 168° obtained under these conditions is a *di-iododinitrobenzene*; if, however, 1 : 3-di-iodobenzene is heated at 80° with a mixture of acetic acid and fuming nitric acid, 2 : 4-di-iodonitrobenzene is the only product. M. A. W.

New Method of Preparing Anilides. F. Bodroux (*Compt. rend.*, 1904, 138, 1427—1429).—The organomagnesium compounds prepared by Meunier (compare Abstr., 1903, i, 544) from a primary amine and a magnesium alkyl haloid condense readily with the esters of monobasic acids to yield the corresponding mono-substituted derivative of the acid amide, according to the equations : $2NHR{\cdot}MgI + R'{\cdot}CO_2R'' = MgI{\cdot}OR'' + R'C(NHR)_2{\cdot}O{\cdot}MgI$; $R'C(NHR)_2{\cdot}OMgI + HCl = NH_2R + MgClI + R'{\cdot}CO{\cdot}NHR$. The ester is added to an ethereal solution of the compound $NHR{\cdot}MgI$, and the resulting compound decomposed by dilute hydrochloric acid ; the yield is almost quantitative. The following substituted amides were thus prepared : formanilide, formo-β-naphthalide, acetanilide, aceto-*p*-toluidide; aceto-β-naphthalide ; propionanilide ; propiono-*o*-toluidide ; propiono-*p*-toluidide ; benzanilide ; benzo-*o*-toluidide ; salicylanilide, and salicyl-*p*-toluidide. M. A. W.

5-Nitro-2-aminotoluene-ω-sulphonic Acid. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 150366).—*o*-Chlorotoluene-ω-sulphonic acid, prepared by boiling *o*-chlorobenzyl chloride with sodium hydrogen sulphite, may be nitrated in sulphuric acid solution, forming 2-*chloro-5-nitrotoluene-ω-sulphonic acid*, the *sodium* salt of which forms yellow, sparingly soluble needles. When heated with ammonia at 150°, yellow crystals of *ammonium 5-nitro-2-aminotoluene-ω-sulphonate* are formed. The chlorine atom may also be replaced by amino-residues by heating with amines. The *sodium* salts of 5-*nitro-2-anilino-*

toluene-ω-sulphonic acid and of the corresponding o- and p-*toluidino-acids* are described. C. H. D.

Aromatic Derivatives of Oxamide and Carbanilide. Paul Camill Taussig (*Monatsh.*, 1904, 25, 375—390).—When a mixture of oxanilide and mercuric oxide is heated at 350° in a slow current of carbon dioxide, 20—25 per cent. of the oxanilide is converted into carbanilide. With oxalyl-*o*-toluidide, the reaction takes place at a lower temperature, and a 40—50 per cent. yield of *s*-di-*o*-tolylcarbamide is obtained.

The action of bromine (2 mols.) on oxalyl-*o*-toluidide (1 mol.) in hot saturated glacial acetic acid solution leads to the formation of *di*-m-*bromo*-o-*oxalyltoluidide*, $C_2O_2(NH\cdot C_7H_6Br)_2$, which crystallises in white, glistening needles, melts at 254—255°, and is soluble in benzene, toluene, or boiling aniline or nitrobenzene. When hydrolysed with alcoholic potassium hydroxide, it yields *m*-bromo-*o*-toluidine (Wroblewski, *Annalen*, 1873, 168, 162). The action of bromine on excess of oxalyl-*o*-toluidide leads to the formation of m-*bromo*-o-*oxalyltoluidide*, $C_7H_7\cdot NH\cdot C_2O_2\cdot NH\cdot C_7H_6Br$, which crystallises in matted, slender needles, melts at 186°, and is soluble in alcohol. Both bromine compounds distil without decomposition. 2 : 2′ : 3 : 3′-Tetramethylcarbanilide is obtained by heating *oxalyl*-as-*xylidide* with mercuric oxide. Di-*m*-tolylcarbamide, formed by heating *m*-toluidine with carbamide or by distilling oxalyl-*m*-toluidide with mercuric oxide, melts at 221°.

o-*Tolidine oxalate*, $(C_7H_8N)_2,C_2H_2O_4$, formed from *o*-tolidine and oxalic acid in alcoholic solution, crystallises from boiling water in leaflets and melts and decomposes at 215°.

Oxalyl-o-*tolidine*, $\begin{array}{l} C_7H_6\cdot NH\cdot CO \\ | \qquad\quad\;\; | \\ C_7H_6\cdot NH\cdot CO \end{array}$, prepared by boiling *o*-tolidine with ethyl oxalate, crystallises from alcohol, acetone, or glacial acetic acid in white, flocculent aggregates, melts at 335°, and is hydrolysed to *o*-tolidine and oxalic acid by aqueous alkali hydroxide.

Carbonyl-o-*tolidine*, $\begin{array}{l} C_7H_6\cdot NH \\ | \\ C_7H_6\cdot NH \end{array}\!\!>CO$, is formed when an alcoholic solution of *o*-tolidine and carbamide is evaporated to dryness and the residue heated at 125—130°, or when oxalyl-*o*-tolidide is distilled with mercuric oxide. It crystallises from warm concentrated sulphuric acid in small, transparent crystals, melts at 355—358° (370—373°, corr.), and is very stable.

Di-*m*-nitrocarbanilide is formed when crude di-*m*-nitro-oxanilide, prepared by heating *m*-nitroaniline with crystalline oxalic acid, is distilled with mercuric oxide. G. Y.

Behaviour of Magnesium Organo-compounds towards Benzylideneaniline. Max Busch (*Ber.*, 1904, 37, 2691—2694).—Magnesium alkyl haloids interact with alkylidene bases, addition taking place at the ·CH:N grouping; thus, benzylideneaniline acts on magnesium alkyl iodides according to the equations:

$$NPh:CHPh + MgRI = MgI\cdot NPh\cdot CHRPh,$$
$$MgI\cdot NPh\cdot CHRPh + H_2O = NHPh\cdot CHRPh + MgI\cdot OH.$$

a-Anilinoethylbenzene nitrate, prepared by adding dilute nitric acid to the product obtained from magnesium methyl iodide (1 mol.) and benzylideneaniline (1 mol.), separates in glistening needles and melts at 162—163°. The free *base*, NHPh·CHMePh, is a viscid oil which boils at 183° under 20 mm. pressure; the *hydrochloride* crystallises in needles and melts at 184—185°; the *sulphate* crystallises in hexagonal, monoclinic plates and melts at 142—143°. The *nitroso*-derivative,

NO·NPh·CHMePh,

is a brownish-yellow oil; it forms a salt with an alcoholic solution of hydrogen chloride, which yields acetophenone when dissolved in water.

Benzylmethylaniline combines with phenylcarbimide to form a-*phenyl*-b-*phenyl*-b-*phenylethylcarbamide*, NHPh·CO·NPh·CHMePh, which separates from a mixture of ether and light petroleum in tetragonal, transparent plates and melts at 94—95°.

Diphenylanilinomethane hydrochloride, prepared by adding hydrochloric acid to the product obtained by the action of magnesium phenyl iodide on benzylideneaniline, separates in glistening, green needles and melts at 199°; the free *base*, $NHPh\cdot CHPh_2$, is a viscid oil. A. McK.

Electrolytic Preparation of *p*-Aminophenol and its Derivatives. FRIEDRICH DARMSTÄDTER (D.R.-P. 150800).—In the preparation of *p*-aminophenol by the electrolytic reduction of nitrobenzene and other nitro-compounds in which the para-position is unoccupied (Gattermann, Abstr., 1893, i, 566), aniline is also obtained together with the aminophenol when metallic cathodes are employed. This may be avoided by the use of carbon cathodes. A suspension of 100 grams of nitrobenzene in 1 kilogram of 85 per cent. sulphuric acid requires a current density of 4 amperes per sq. dcm. C. H. D.

***p*-Aminophenol-*m*-sulphonic Acid.** KALLE & Co. (D.R.-P. 150982).—p-*Nitroacetylmetanilic acid*, $NHAc\cdot C_6H_3(NO_2)\cdot SO_3H$, prepared by nitrating acetylmetanilic acid, forms heavy, sandy crystals. When heated at 100° in closed vessels with solutions of alkali hydroxides or carbonates, it is converted into a mixture of nitroresorcinol and p-*nitrophenol*-m-*sulphonic acid*, which may be separated by acidifying and extracting the nitroresorcinol with ether or benzene, or by neutralising with acid, when the sparingly soluble monosodium salt of nitroresorcinol is precipitated. The acid yields p-*aminophenol*-m-*sulphonic acid* on reduction. C. H. D.

Action of Zinc Chloride on Acid Esters of Phenols. Acetylcresols. JOHAN F. EIJKMAN (*Chem. Centr.*, 1904, i, 1597; from *Chem. Weekblad*, 1, 453—461).—4-*Acetyl*-m-*cresol* (4-acetyl-3-hydroxytoluene), $C_6H_3MeAc\cdot OH$, prepared by heating a mixture of *m*-cresol and acetyl chloride with zinc chloride for six hours at 140—160°, has an odour similar to that of creosote and forms transparent crystals which melt at 21°; it boils at 103° under 7 mm., at 126° under 20 mm., and at 245° under 760 mm. pressure, has a sp. gr. 1·1012 at 13·1°, n_a 1·5527 at 13·1°, and gives a dark violet coloration with an alcoholic solution of ferric chloride. The *oxime* is readily soluble in benzene

and melts at 103°. The *methyl ether*, $C_{10}H_{12}O_2$, solidifies at 37·2°, boils at 265° under 754 mm. pressure, has a sp. gr. 1·0154 at 78·1°, and n_α 1·50933 at 78·1°. The *oxime* of the methyl ether forms colourless needles, is readily soluble in benzene, and melts at 136°. The *ethyl ether* melts at 71°, boils at 140° under 10 mm. pressure, has a sp. gr. 0·9865 at 78·8° and n_α 1·49989 at 78·8°. The *oxime* of the ethyl ether is readily soluble in benzene and melts at 132°.

6-*Acetyl*-m-*cresol* (6-acetyl-3-hydroxytoluene), $C_6H_3MeAc{\cdot}OH$, prepared by allowing a mixture of *m*-cresol, acetyl chloride, and zinc chloride to remain for several weeks at the ordinary temperature, crystallises from alcohol in white, odourless crystals which melt at 128°; it boils at 313° and does not give a coloration with an alcoholic solution of ferric chloride. The *methyl ether* melts at 12°, boils at 150° under 20 mm. and at 268° under 759 mm. pressure, and has a sp. gr. 1·0867 at 15·7° and n_α 1·5503 at 15·7°. The *ethyl ether* melts at 22°, boils at 155° under 18 mm. and at 195° under 81 mm. pressure, and has a sp. gr. 1·0034 at 77·6° and n_α 1·51242 at 77·6°. 6-Acetyl-*m*-cresol and its ethers do not form oximes.

By the action of an alkaline solution of potassium permanganate on the ethers of 4-acetyl-*m*-cresol and 6-acetyl-*m*-cresol, the following derivatives of glyoxylic acid are formed. 2-*Methoxy*-4-*methylphenylglyoxylic acid*, $OMe{\cdot}C_6H_3Me{\cdot}CO{\cdot}CO_2H$, prepared from the methyl ether of 4-acetyl-*m*-cresol, melts at 101°. 2-*Ethoxy*-4-*methylphenylglyoxylic acid* melts at 144°. 4-*Methoxy*-2-*methylphenylglyoxylic acid*, obtained by oxidising the methyl ether of 6-acetyl-*m*-cresol, melts at 85°. 4-*Ethoxy*-2-*methylphenylglyoxylic acid* melts at 78°. All the preceding α-ketonic acids crystallise from benzene and, with the exception of 2-ethoxy-4-methylphenylglyoxylic acid, from water or dilute alcohol with $1H_2O$. The corresponding toluic acids are obtained by further oxidation of the acids with manganese dioxide and a 50 per cent. solution of acetic acid, or with glacial acetic acid and a 4 per cent. solution of potassium permanganate.

2-*Methoxy*-p-*toluic acid*, $OMe{\cdot}C_6H_3Me{\cdot}CO_2H$, melts at 104°. 2-Ethoxy-*p*-toluic acid melts at 78·5° (compare Paternò and Canzoneri, *Jahresber.*, 1879, 519). 4-*Methoxy*-o-*toluic acid* melts at 176°. 4-*Ethoxy*-o-*toluic acid* melts at 146°.

By the action of excess of hydrogen peroxide on the α-ketonic acids, 2-*methoxyterephthalic acid*, 2-*ethoxyterephthalic acid*, 4-*methoxyphthalic acid*, and 4-*ethoxyphthalic acid* are formed; the acids melt at 281°, 254°, 167°, and 163° respectively. By the action of zinc chloride and acetyl chloride on resorcinol, acetylresorcinol, $C_6H_3Ac(OH)_2$, and diacetylresorcinol, $C_6H_2Ac_2(OH)_2$, are formed, whilst under similar conditions thymol yields only *p*-acetyl-*o*-thymol, $C_6H_2MePrAc{\cdot}OH$.

E. W. W.

Cyclic Compounds. GEORGE STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 485—489. Compare Markownikoff and Stadnikoff, Abstr., 1903, i, 803).—On heating the heptanaphthylene oxide previously described (*loc. cit.*) with water, it yields *methyl*cyclo*hexane*-3 : 4-*glycol*, $CHMe{<}\begin{matrix}CH_2\text{——}CH_2\\CH_2{\cdot}CH(OH)\end{matrix}{>}CH{\cdot}OH$, which is a viscous, colourless, odour-

less liquid boiling at 134° under 18 mm. pressure. The *diacetyl* derivative, $C_7H_{12}(OAc)_2$, is a viscous liquid which has a pleasant fruity odour and boils at 157—158° under 40 mm. pressure.

Heptanaphthylene dibromide, $C_7H_{12}Br_2$, is a colourless liquid which has a camphor-like odour, boils at 130° under 40 mm. pressure, and has a sp. gr. 1·56 at 15°/15° and 1·648 at 20°/15°, and $[\alpha]_D$ 18°48′36″.

The chloro-ketone prepared by oxidising the chlorohydrin by means of chromic acid boils at 110—111° under 40 mm. pressure, and not at 114° as previously stated (*loc. cit.*), and has a sp. gr. 1·106 at 15°/15°.

T. H. P.

Synthesis of a New Series of Tertiary Alcohols from *cyclo*-Hexanol. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1904, 138, 1321—1324).—Tertiary alcohols of the type

$$CH_2{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}CR\cdot OH$$

are readily obtained from *cyclo*hexanone (compare Sabatier and Senderens, this vol., i, 156) by means of the Grignard reaction. These alcohols are insoluble in water, readily soluble in alcohol or ether, and are converted by the action of dehydrating agents into the corresponding olefine, the constitution of which is not at present determined. The following alcohols and olefines were prepared: methyl*cyclo*hexanol (compare Markownikoff and Tcherdintzeff, Abstr., 1900, i, 578) boils at 68° under 20 mm. pressure and has a sp. gr. 0·953 at 0°/0°; the *acetyl* derivative boils at 176° under 760 mm. pressure, and the *phenylurethane*, $C_6H_{10}MeO\cdot CO\cdot NHPh$, crystallises in bright needles and melts at 105°; by the action of anhydrous zinc chloride at 160°, an *olefine* is obtained boiling at 108° under 760 mm. pressure and having a sp. gr. 0·827 at 0°/0°. *Ethyl*cyclo*hexanol*, $C_6H_{10}Et\cdot OH$, has an odour of camphor, forms brilliant prisms which melt at 33°, boils at 76° under 20 mm. and at 166° under 760 mm. pressure; the *acetyl* derivative boils at 190° under 760 mm. pressure, and the *phenylurethane* melts at 83°; the *olefine* obtained by the action of zinc chloride boils at 134° under 760 mm. pressure. *Propyl*cyclo*hexanol*, $C_6H_{10}Pr\cdot OH$, is a viscous liquid with an odour like camphor, it boils at 85° under 20 mm. and at 180° under 760 mm. pressure, has a sp. gr. 0·945 at 0°/0°, and yields an *olefine* boiling at 154° under 760 mm. pressure. iso*Butyl*cyclo*hexanol*,

$$OH\cdot C_6H_{10}\cdot CH_2\cdot CHMe_2,$$

boils at 102° under 20 mm. pressure. iso*Amyl*cyclo*hexanol*, $OH\cdot C_6H_{10}\cdot C_5H_{11}$, is a viscous liquid smelling of camphor, boils at 115° under 20 mm. pressure, has a sp. gr. 0·917 at 0°/0°, and yields an *olefine* boiling at 194° under 760 mm. pressure and having a sp. gr. 0·856 at 0°/0°. *Phenyl*cyclo*hexanol*, $C_6H_{10}Ph\cdot OH$, has an agreeable aromatic odour, forms large, thick crystals which melt at 61°, boils at 153° under 20 mm. pressure, and yields an *olefine* boiling at 133° under 20 mm. pressure and having a sp. gr. 1·004 at 0°/0°. p-*Tolyl*cyclo*hexanol*, $OH\cdot C_6H_{10}\cdot C_7H_7$, is a liquid with an aromatic odour, boils at 151° under 20 mm. pressure, has a sp. gr. 0·995 at 0°/0°, forms colourless crystals melting at 0°, and yields an *olefine* boiling at 142° under 20 mm. pressure and having a sp. gr. 0·981 at 0°/0°. *Benzyl*-

cyclo*hexanol*, $OH\cdot C_6H_{10}\cdot CH_2Ph$, forms colourless crystals melting at 33°, boils at 160° under 20 mm. pressure, and yields an *olefine* boiling at 138° under 20 mm. pressure and having a sp. gr. 0·983 at 0°/0°. cyclo*Hexyl*cyclo*hexanol*, $OH\cdot C_6H_{10}\cdot C_6H_{11}$, forms white, pearly plates which melt at 51°, boils with decomposition at 148° under 20 mm. pressure, and yields an *olefine* boiling at 124° under 20 mm. pressure and having a sp. gr. 0·923 at 0°/0°. M. A. W.

Reduction of *o*-Nitrobenzyl Alcohol. General Remarks on the Formation of Indazyl Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1904, 138, 1425—1427).—The author summarises the results already published (compare Abstr., 1903, i, 371, 585; this vol., i, 121, 351). *Indazyl-*o*-benzyl acetate* forms red needles melting at 39—40° and is decomposed on distillation into phenylindazole and acetic acid.

M. A. W.

Cholesterol. II. ADOLF WINDAUS (*Ber.*, 1904, 37, 2027—2032. Compare this vol., i, 49).—The oxidation of cholestandione, $C_{27}H_{42}O_2$, to cholestanonic acid, $C_{27}H_{42}O_5$, was regarded as analogous to the oxidation of camphor to camphoric acid; confirmation of the view that cholestandione is a cyclic ketone has been obtained by isolating the intermediate products of oxidation, which are analogous to those obtained from suberone.

The intermediate *ketohydroxy-acid*, $C_{27}H_{44}O_4$, prepared by oxidising cholestandione with ammonium persulphate, crystallises from hot acetic acid in prisms, sinters at 185°, and melts at 217°; the sintering is characteristic of the purified acid and is probably due to gradual conversion into the lactone. The *sodium* salt, $C_{27}H_{43}O_4Na$, crystallises from 50 per cent. alcohol in large, glistening plates. The *methyl* ester, $C_{28}H_{46}O_4$, separates from petroleum in minute crystals melting at 105°, but does not crystallise at all readily; its *oxime*, $C_{28}H_{47}O_4N$, however, crystallises readily from methyl alcohol in glistening plates and melts at 148°. The acid is oxidised by chromic acid to cholestanonic acid, showing that the hydroxyl group is in the condition of a primary alcohol.

Dibromocholestandione, $C_{27}H_{40}O_2Br_2$, crystallises from 80 per cent. alcohol in stout, colourless prisms, and, when rapidly heated, blackens and melts, liberating gas, at about 165°.

Bromocholestanonic acid, $C_{27}H_{41}O_5Br$, crystallises from 80 per cent. alcohol in lustrous scales, similar to cholesterol, and darkens and melts with liberation of gas at about 151°. T. M. L.

Action of Magnesium Aryl Haloids on Dicarboxylic Acids. WALTHER DILTHEY and E. LAST (*Ber.*, 1904, 37, 2639—2641. Compare Valeur, Abstr., 1901, i, 317; Gattermann and Maffezzoli, this vol., i, 172).—The action of bromobenzene and magnesium on ethyl oxalate in ethereal solution leads to the formation of β-benzopinacolin, on ethyl succinate in ethereal solution, to the formation of the *glycol*, $OH\cdot CPh_2\cdot CH_2\cdot CH_2\cdot CPh_2\cdot OH$, which crystallises in needles, melts at 202°, is soluble in alcohol or glacial acetic acid, and dissolves in concentrated sulphuric acid to a red solution.

The *hydroxy-ketone*, $OH\cdot CPh_2\cdot CH_2\cdot COPh$, is obtained when phenyl magnesium bromide is boiled with ethyl malonate in ethereal solution

and the product treated with acidified ice-water. It crystallises in transparent, colourless nodules, melts and decomposes into acetophenone and benzophenone at 126—127°, decomposes into the same substances when recrystallised from petroleum boiling above 130°, dissolves in concentrated sulphuric acid to a red solution, and forms a yellowish-red solution with hydrogen chloride and stannic chloride in benzene or chloroform solution. G. Y.

Action of Magnesium Methiodide on Piperonal. EFISIO MAMELI (*Gazzetta*, 1904, 34, i, 358—374).—The action of magnesium methiodide on piperonal yields methylpiperonyl ether, methylpiperonyl alcohol, acetopiperone, piperonylethylene, and a polymeride of the last-named compound.

Methylpiperonylcarbinol (β-3 : 4-*methylenedioxyphenylethyl alcohol*), $CH_2{:}O_2{:}C_6H_3{\cdot}CHMe{\cdot}OH$, is an oily liquid insoluble in water, but soluble in ether or benzene, and having an odour recalling that of heliotrope; it boils at 139—140° under 22 mm. pressure, partially decomposing into water and piperonylethylene; it has the normal molecular weight in freezing benzene, and on oxidation with permanganate yields acetopiperone; with concentrated sulphuric acid, it gives instantly a solid violet mass, which afterwards becomes purple.

Piperonylethylene (3 : 4-*methylenedioxystyrene*),

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{:}CH_2,$$

distils at 108—109° under 20—22 mm. and at 223—225° under the ordinary pressure, being partially transformed in both cases into the polymeride (see *infra*); it does not mix with water, has a peculiar odour and a neutral reaction, and is soluble in benzene or chloroform; it distils in a current of steam and has the normal molecular weight in freezing benzene or acetic acid; it rapidly decolorises bromine and absorbs hydrogen bromide, and with potassium permanganate it yields piperonylic acid; sulphuric acid converts it into a pasty, amorphous mass of a wine-red or violet-red colour; its sp. gr. is 1·158 at 15°; on keeping about a month, it becomes transformed into a gelatinous, viscous mass having the same composition and molecular weight as the original compound. On treatment with hydrogen bromide, it yields *piperonylmonobromoethane* (α-3 : 4-*methylenedioxyphenyl-α-bromoethane*), $CH_2{:}O_2{:}C_6H_3{\cdot}CHBrMe$, which crystallises from benzene or a mixture of benzene and light petroleum in tufts of white prisms melting at 107°. With bromine, it gives *piperonyldibromoethane*, $CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CH_2Br$, crystallising from benzene in spheroidal agglomerates of slender, white needles melting at 160° and dissolving in alcohol.

The polymeride of piperonylethylene, when heated rapidly, begins to fuse and decompose at 210°, bubbles being evolved which increase up to 230° and then diminish, after which a yellow, glassy mass remains.

Dipiperonyldiethyl ether (?), $O(CHMe{\cdot}C_6H_3{:}O_2{:}CH_2)_2$, crystallises from alcohol in tufts of white prisms melting at 111°; it dissolves in benzene or chloroform and to a slight extent in water or ether; it slightly reduces Fehling's solution, but not ammoniacal silver nitrate;

at low concentrations, it gives low values for the molecular weight in benzene, but exhibits normal behaviour in stronger solutions.

T. H. P.

Synthesis of Aromatic Fatty Acids by means of Lactones. JOHAN F. EIJKMAN (*Chem. Centr.*, 1904, i, 1416; from *Chem. Weekblad*, 1, 421—424).—By the action of γ-valerolactone, $\begin{matrix} CH_2\text{——}CO \\ | \\ CH_2{\cdot}CHMe \end{matrix}\!\!>\!O$, on benzene in presence of aluminium chloride, γ-*phenylvaleric acid*, $CHMePh{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, is obtained. This acid forms colourless crystals, melts at about 13°, boils at 147° under 2 mm., at 170° under 10 mm., or at 210° under 85 mm. pressure, and has a sp. gr. 1·0554 at 15°. The *aluminium* salt, $Al(C_{11}H_{13}O_2)_3$, forms a white, curdy mass. The *calcium* salt is an amorphous precipitate which is soluble in alcohol or ether, but only sparingly so in water. γ-*Tolylvaleric acid*, $C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, prepared in a similar manner by the action of toluene on γ-valerolactone, is a colourless, syrupy liquid which boils at 154° under 2 mm. and at 176° under 10 mm. pressure; it has a sp. gr. 1·0398 at 15°. γγ-*Diphenylbutyric acid*,

$$CHPh_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

obtained by the action of benzene on γ-phenylbutyrolactone in presence of aluminium chloride, crystallises from alcohol in colourless crystals melting at 107°.

E. W. W.

ω-Cyanodimethylaniline. THEODOR ST. WARUNIS and FRANZ SACHS (*Ber.*, 1904, 37, 2636—2639. Compare Abstr., 1902, i, 780; 1903, i, 335, 336).—ω-*Cyanodimethylaniline*, $C_6H_5{\cdot}NMe{\cdot}CH_2{\cdot}CN$, prepared by heating methylaniline and formaldehydecyanohydrin in a sealed tube at 100° and fractionally distilling the product, forms a colourless liquid, becoming dark, and boiling at 266°. On dissolving in concentrated sulphuric acid, pouring into water, and adding ammonia, phenylmethylglycineamide, $NMePh{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, is precipitated, and crystallises from water in white prisms melting at 163° (compare Silberstein, Abstr., 1885, 160); it yields phenylmethylglycine on hydrolysis.

Sodium nitrite and hydrochloric acid convert the nitrile into p-*nitroso-ω cyanodimethylaniline*, $NO{\cdot}C_6H_4{\cdot}NMe{\cdot}CH_2{\cdot}CN$, separating from alcohol in green crystals and melting at 114—116°. *p*-Nitrobenzyl cyanide forms the *compound*

$$NO_2{\cdot}C_6H_4{\cdot}C(CN){:}N{\cdot}C_6H_4{\cdot}NMe{\cdot}CH_2{\cdot}CN,$$

separating from dilute alcohol in bright red crystals and melting at 195°.

Nitrous acid converts the glycineamide into *methyl*-p-*nitrosophenylglycineamide*, $NO{\cdot}C_6H_4{\cdot}NMe{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, melting at 179°, sparingly soluble in alcohol, insoluble in ether or benzene. Malononitrile forms an *azomethine* compound melting at 211°; *p*-nitrobenzyl cyanide forms a brown *compound* melting at 229°.

Nitrous acid also reacts with anilinoacetonitrile to form a *nitrosoamine* melting at 51—52°. The *nitrosoamine* of anilinoacetamide, $NO{\cdot}NPh{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, crystallises from water and melts at 143°.

C. H. D.

Halogen Derivatives of Phenylglycine-*o*-carboxylic Acid. Badische Anilin- & Soda-Fabrik (D.R.-P. 148615).—Halogen derivatives of phenylglycine-*o*-carboxylic acid are readily obtained by the action of halogens on phenylglycine-*o*-carboxylic acid suspended in glacial acetic acid.

Bromophenylglycine-o-*carboxylic acid* crystallises from alcohol in yellow needles and melts at 228°.

Chlorophenylglycine-o-*carboxylic acid* melts at 210—215°. The addition of a further quantity of bromine causes no further substitution in the cold, but the continued passage of chlorine leads to the formation of *dichlorophenyl*-o-*carboxylic acid*, melting at 237—238°.

The same derivatives are obtained by the action of chlorine or bromine on ω-cyanomethylanthranilic acid and hydrolysis of the products. *Bromo-ω-cyanomethylanthranilic acid* forms yellow needles and melts at 209—210°, *chloro-ω-cyanomethylanthranilic acid* melts at 199—200°, and *dichloro-ω-cyanomethylanthranilic acid* at 222—223°.

C. H. D.

Products of the Hydrolysis of Ethyl 3:5-Dinitrobenzoylacetoacetate. Ludwig Berend and Fritz Heymann (*J. pr. Chem.*, 1904, [ii], 69, 449—473. Compare Abstr., 1902, i, 470).—3:5-Dinitrobenzoyl chloride boils at 196° under 10—12 mm. pressure.

When treated with 10 per cent. alcoholic ammonia, ethyl 3:5-dinitrobenzoylacetoacetate yields 3:5-dinitrobenzamide melting at 183°, ethyl 3:5-dinitrobenzoylacetate, and the ammonium compound of the latter substance.

Ethyl 3:5-*dinitrobenzoylacetate* crystallises from alcohol in white leaflets and melts at 73°. On evaporation of the alcoholic mother liquor, crystals are obtained which melt at about 173° and on recrystallisation yield the leaflets melting at 73°. The *ammonium* compound is only slightly soluble in water.

When warmed with hydroxylamine hydrochloride and sodium acetate in concentrated aqueous solution, ethyl 3:5-dinitrobenzoyl acetate yields 3-s-*dinitrophenyl*isoo*xazolone*, $O<\begin{matrix}N{=}C\cdot C_6H_3(NO_2)_2\\ CO\cdot CH_2\end{matrix}$, which crystallises in prismatic needles and melts and decomposes at 173—175°.

With phenylhydrazine in glacial acetic acid solution, ethyl 3:5-dinitrobenzoylacetate forms 1-*phenyl*-3-s-*dinitrophenyl-5-pyrazolone*,

$$NPh<\begin{matrix}N{=}C\cdot C_6H_3(NO_2)_2\\ CO\cdot CH_2\end{matrix},$$

which crystallises in slender, yellow needles and melts at 227°.

When boiled with 30—40 per cent. sulphuric acid, ethyl 3:5-dinitrobenzoylacetoacetate yields 3:5-dinitrobenzoylacetone and 3:5-dinitroacetophenone.

3:5-*Dinitrobenzoylacetone* crystallises in glistening needles and melts at 121°. With hydrazine hydrate in alcoholic solution, it yields 3-s-*dinitrophenyl-5-methylpyrazole*, which crystallises in slender, white needles and melts at 220°.

With phenylhydrazine in glacial acetic acid solution, 3:5-dinitro-

benzoylacetone forms 1-*phenyl*-3-s-*dinitrophenyl*-5-*methylpyrazole*, which crystallises in rhombic plates and melts at 179°.

3 : 5-Dinitroacetophenone forms an *oxime* which crystallises in white needles and melts at 122°. m-*Nitrobenzylidene*-3 : 5-*dinitroacetophenone*, $NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot C_6H_3(NO_2)_2$, formed by the action of *m*-nitrobenzaldehyde on 3 : 5-dinitroacetophenone, is a yellow, crystalline powder which melts at 226°.

3-*Nitro*-5-*aminoacetophenone*, obtained by reduction of dinitroacetophenone with the calculated amount of stannous chloride and hydrochloric acid, crystallises in stellate clusters of needles and melts at 156—158°.

Diacetyldiaminoacetophenone crystallises in white needles, melts at 210°, and is formed by the action of acetic anhydride on 3 : 5-*diaminoacetophenone*, which crystallises according to the solvent in clear yellow plates, thick prisms, or stellate groups of needles, and melts at 133—134°. G. Y.

Action of Mixed Organomagnesium Compounds on Phthalimide and Phenylphthalimide. II. CONSTANTIN BÉIS (*Compt. rend.*, 1904, 139, 61—62).—The author discusses the two possible formulæ for the product of the reaction between magnesium ethyl bromide and phthalimide,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CEt}}{>}N \quad \text{or} \quad C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{C(CHMe)}}{>}NH,$$

obtained by the loss of a molecule of water from the intermediate 3-hydroxy-3-ethyl*iso*indolinone, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CEt(OH)}}{>}NH$ (compare this vol., i, 503); in favour of the first formula, it is pointed out that in the case of the substituted phthalimides the hydroxy*iso*indolinone is always obtained (compare Sachs and Ludwig, this vol., i, 266). The author, however, inclines to the second or *iso*indolone formula for the following reasons: (1) when the radicle introduced by the organomagnesium compound cannot form an ethylene linking with the carbon atom carrying the hydroxyl group, dehydration does not take place, and the hydroxy-compound is obtained; thus, with phthalimide, magnesium phenyl bromide gives 3-*hydroxy*-3-*phenyl*iso*indolinone*,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CPh(OH)}}{>}NH,$$

melting at 160°, soluble in hot water and in the ordinary organic solvents; (2) *iso*butyl*iso*indolone reacts with magnesium ethyl bromide in the normal manner of compounds containing an NH group; (3) ethyl*iso*indolone and *iso*butyl*iso*indolone behave like imides in giving silver derivatives of the type $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{C(CHMe)}}{>}NAg$. M. A. W.

3-Aminophthalanil. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Ber.*, 1904, 37, 2610—2612. Compare Abstr., 1903, i, 700).—3-*Aminophthalanil*, $NH_2\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}NPh$, prepared by reducing the nitro-compound with iron and acetic acid, crystallises from acetic acid in long, yellow needles and melts at 180—186°; when crystallised from benzene, it melts at 185—187°. The *acetyl* derivative, $C_{16}H_{12}O_3N_2$,

crystallises from alcohol in white needles and melts at 191°; unlike the base, it does not give fluorescent solutions. T. M. L.

Thermochromic Properties of Dibenzylidenesuccinic Anhydride. (Butandiene Compounds, IV.) HANS STOBBE [and, in part, VICTOR VON VIGIER] (*Ber.*, 1904, 37, 2465—2468).—Dibenzylidenesuccinic anhydride, $\begin{matrix} CHPh{:}C{\cdot}CO \\ CHPh{:}\overset{|}{C}{\cdot}CO \end{matrix}{>}O$ (this vol., i, 589), forms large, triclinic crystals melting at 203—204°, and lemon-yellow in colour at the ordinary temperature. When cooled to $-80°$, the colour becomes distinctly lighter, and at $-180°$ in liquid air is a pale sulphur-yellow. The darker yellow colour is gradually restored on warming to the ordinary temperature. On heating, darkening is first observed at 80°, a distinct orange tint is perceptible at 100°, and a brown colour at 160°. The original yellow colour is rapidly restored on cooling. Prolonged heating at 160° produces a further change, and the substance becomes permanently lighter yellow on cooling.

The colour changes are similar to those observed in zinc oxide, potassium chromate, and mercuric cuprous iodide, and occur only in the solid state. Solutions of dibenzylidenesuccinic anhydride in benzene, anisole, and phenetole have the same colour when cold or when boiling. The molecular weight in boiling chloroform and boiling naphthalene is also constant, the compound being in both cases unimolecular. C. H. D.

Triarylbutadienedicarboxylic Acids. (Butadiene Compounds. V.) HANS STOBBE [with PAUL KOHLMANN, PHOKION NAOÚM, and KURT KOHLMANN] (*Ber.*, 1904, 37, 2656—2662. Compare Abstr., 1897, i, 192). —γγ-Diphenyl-α-benzylideneitaconic acid (αδδ-triphenylbutadiene-βγ-dicarboxylic acid) is prepared by the condensation of benzaldehyde with ethyl γγ-diphenylitaconate by means of sodium ethoxide in alcoholic solution. The acid obtained from the aqueous solution of the sodium salt is white and contains $9H_2O$, which is gradually lost at the ordinary temperature, the substance becoming yellow. When crystallised from chloroform, the acid forms white, hexagonal prisms containing chloroform of crystallisation; these crystals rapidly lose chloroform on exposure to air, and become yellow. This yellow acid is found to melt and decompose at 218—219°, and may be the stable modification of the acid melting at 207° (*loc. cit.*). The sodium, calcium, *barium*, and *piperidine* salts are described. The *anhydride*, $C_{24}H_{16}O_3$, formed by the action of acetyl chloride, crystallises in red prisms and melts, but does not decompose, at 218°. Oxidation of γγ-diphenyl-α-benzylideneitaconic acid with potassium permanganate in aqueous potassium carbonate solution leads to the formation of benzophenone and benzoic and oxalic acids.

*γγ-Diphenyl-α-*p*-toluylideneitaconic acid,*

$$C_7H_7{\cdot}CH{:}C(CO_2H){\cdot}C(CO_2H){:}CPh_2,$$

obtained from *p*-tolualdehyde and ethyl diphenylitaconate, crystallises in short, yellow prisms or plates, melts at 231°, and dissolves in concentrated sulphuric acid to an orange solution, which becomes green and finally red. The *sodium* salt contains water of crystallisation; the *anhydride*, formed by the action of acetyl chloride on the acid, crystallises in red needles and melts at 194°.

δδ-Diphenyl-α-cumylbutadiene-αγ-dicarboxylic acid,

$$C_6H_4Pr^{\beta}\cdot CH{:}C(CO_2H)\cdot C(CO_2H){:}CPh_2,$$

from cuminaldehyde and ethyl diphenylitaconate, crystallises in short, thick, yellow prisms and melts and decomposes at 229°. The *sodium* salt contains $3H_2O$ and crystallises in white plates; the *anhydride* crystallises in red prisms and melts at 139—140°. G. Y.

Formation of Stereoisomeric Butanedicarboxylic Acids by Reduction of Butadienedicarboxylic Acids. (Butadiene Compounds. VI.) Hans Stobbe and Victor von Vigier (*Ber.*, 1904, **37**, 2662—2670).—Dibenzylidenesuccinic acid is reduced by sodium amalgam in presence of carbon dioxide in aqueous solution to a mixture of *cis*- and *trans*-dibenzylsuccinic acids, the *cis*-acid being the main product. These stereoisomeric acids are separated with difficulty by crystallisation from water or ether. The *trans*-acid is the main product obtained on reduction of *iso*dibenzylidenesuccinic acid.

cis-*Dibenzylsuccinic acid*, $\begin{array}{ccc} & CO_2H & CO_2H \\ & | & | \\ H\cdot & C —— & C\cdot H \\ & | & | \\ & C_7H_7 & C_7H_7 \end{array}$, crystallises in sheaves of needles, melts and decomposes at 203°, and dissolves in concentrated sulphuric acid to a colourless solution which gradually becomes rose-coloured. The *anhydride* formed by the action of acetyl chloride on the acid crystallises in leaflets and melts at 104°.

trans-*Dibenzylsuccinic acid*, $\begin{array}{ccc} & CO_2H & C_7H_7 \\ & | & | \\ H\cdot & C —— & C \\ & | & | \\ & C_7H_7 & CO_2H \end{array}$, crystallises in monoclinic prisms, melts at 204°, decomposes at 207°, and dissolves in concentrated sulphuric acid to a yellowish-green solution. The *anhydride* crystallises in small, six-sided prisms and melts at 155°.

A mixture of the two acids melts at 195° and decomposes at 204°. The *cis*-acid is converted into the *trans*-form when heated with concentrated hydrochloric acid at 180°. Both anhydrides undergo partial isomeric change when heated at 180°.

Reduction of γ-diphenyl-α-benzylideneitaconic acid with sodium amalgam in presence of carbon dioxide in aqueous solution leads to the formation of a mixture of *cis*- and *trans*-αδδ-triphenylbutane-βγ-dicarboxylic acids, which melts at 175—191° and is resolved into its components when recrystallised from a mixture of ether and low boiling petroleum.

cis-αδδ-*Triphenylbutane-βγ-dicarboxylic acid*, $\begin{array}{ccc} & CO_2H & CO_2H \\ & | & | \\ H\cdot & C —— & C\cdot H \\ & | & | \\ & CH_2Ph & CHPh_2 \end{array}$, crystallises in hair-like needles, melts at 175°, and is almost completely converted into the *trans*-modification when heated with concentrated hydrochloric acid at 180°. The trans-*acid* crystallises in prisms and melts at 205°. G. Y.

Methyl Hydrogen Phthalonate. Arthur Glogau (*Monatsh.*, 1904, **25**, 391—396. Compare this vol., i, 249).—Concentrated alcoholic ammonia hydrolyses methyl hydrogen phthalonate (m. p.

79—81°). The action of cold concentrated aqueous ammonia on the ester leads to the formation of *iminophthalonamic acid*,

$$NH_2\cdot CO\cdot C(NH)\cdot C_6H_4\cdot CO_2H$$

or $NH_2\cdot CO\cdot C_6H_4\cdot C(NH)\cdot CO_2H$, and its *ammonium* salt. The acid crystallises in slender, colourless needles and melts at 191—193°; the ammonium salt melts and decomposes at 218—223° and is insoluble in dilute, aqueous ammonia; the *mercuric* salt is formed as a white precipitate on addition of mercuric chloride in aqueous solution.

The action of bromine and potassium hydroxide on phthalonic acid and on iminophthalonamic acid leads to the formation of phthalic acid in both cases.

With phenylhydrazine in methyl alcoholic solution, methyl hydrogen phthalonate yields Henrique's methyl phenylphthalazonecarboxylate, which melts at 114° (Abstr., 1888, 824).

The methyl hydrogen phthalonate, which melts at 79—81°, must have the constitution $CO_2H\cdot C_6H_4\cdot CO\cdot CO_2Me$. G. Y.

Substituted Benzaldehydes. 2-Chloro-5-nitrobenzaldehyde and *ortho*-Dimethylaminobenzaldehyde. PAUL COHN and ALBERT BLAU (*Monatsh.*, 1904, **25**, 365—374).—Reduction of 2-chloro-5-nitrobenzaldehyde (Erdmann, Abstr., 1893, i, 160) with sodium hydrogen sulphite and hydrochloric acid leads to the formation of 2-*chloro*-5-*aminobenzaldehyde hydrochloride*, which is amorphous. 2-*Chloro*-5-*acetylaminobenzaldehyde* crystallises in glistening, white needles and melts at 163—164°. With dimethylamine in alcoholic solution, 2-chloro-5-nitrobenzaldehyde forms 5-*nitro*-2-*dimethylaminobenzaldehyde*, which crystallises in yellow needles and melts at 105°. The *oxime* crystallises in yellow needles and melts at 125°; the *phenylhydrazone* crystallises in dark red needles and melts at 168°; the *hydrochloride* is easily soluble in water; the *platinichloride* is unstable. When boiled with primary aromatic bases in alcoholic solution, 2-chloro-5-nitrobenzaldehyde yields benzylidene derivatives. 2-*Chloro*-5-*nitrobenzylideneaniline* crystallises in yellow needles and melts at 103°; 2-*chloro*-5-*nitrobenzylidene*-p-*toluidine* crystallises in yellow leaflets and melts at 133°; *chloronitrobenzylidene*-o-*toluidine* crystallises in glistening scales and melts at 125°; *chloronitrobenzylidene*-α-*naphthylamine* crystallises in yellow needles, melts at 176°, and is only slightly soluble in alcohol.

o-*Dimethylaminobenzaldehyde*, formed by the action of methyl sulphate on *o*-aminobenzaldehyde (Abstr., 1903, i, 492), boils at 142° under 30 mm., at 244° under atmospheric pressure. The *platinichloride* crystallises in brown needles; the *oxime* crystallises in white needles and melts at 84—85°; the *azine*,

$$NMe_2\cdot C_6H_4\cdot CH:N\cdot N:CH\cdot C_6H_4\cdot NMe_2,$$

crystallises in yellow needles, melts at 148—149°, and forms a crystalline *platinichloride*.

Di-o-*aminobenzylideneazine*, obtained from *o*-aminobenzaldehyde and hydrazine sulphate, crystallises in yellow needles and melts at 248°.

G. Y.

Amino-ketones. ERICH KOLSHORN (*Ber.*, 1904, 37, 2474—2486). —*Phthalimidomethyl ethyl ketone*, $C_6H_4{:}(CO)_2{:}N{\cdot}CH_2{\cdot}COEt$, prepared by heating chloromethyl ethyl ketone with potassium phthalimide in xylene solution at 135°, crystallises from boiling water in colourless, glistening needles melting at 107°; on heating it with 20 per cent. hydrochloric acid, the *hydrochloride* of *aminomethyl ethyl ketone* is formed, which crystallises in hygroscopic, rhombic plates melting at about 152°; the *platinichloride* melts at 169—170°. Aminomethyl ethyl ketone acts as a powerful reducing agent towards Fehling's, and with phenylhydrazine forms the ethylglyoxalphenylethylosazone described by Woff (Abstr., 1896, i, 87). It unites with potassium thiocyanate, forming 4-*ethylglyoxaline-2-mercaptan*, $\begin{array}{l}\mathrm{CEt{\cdot}NH}\\ \|\\ \mathrm{CH{-}{-}N}\end{array}\!\!>\!\mathrm{C{\cdot}SH}$ or $\begin{array}{l}\mathrm{CEt{-}N}\\ \|\\ \mathrm{CH{\cdot}NH}\end{array}\!\!>\!\mathrm{C{\cdot}SH}$, which crystallises in colourless plates and on heating softens at 210°, and is not melted by 265°. From this, α- or β-*ethylglyoxaline* is formed on oxidation with nitric acid, of which the following salts are described: the *nitrate*, forming colourless plates, which soften at 78° and melt at 82·5°; the *aurichloride*, crystallising in thin needles, often in stellar aggregates, melting at 118—119°; and the *picrate* melting at 116°. When condensed with potassium cyanate, 2-*hydroxy-4-ethylglyoxaline*, $\begin{array}{l}\mathrm{CEt{-}{-}N}\\ \|\\ \mathrm{CH{\cdot}NH}\end{array}\!\!>\!\mathrm{C{\cdot}OH}$, is formed; this darkens at 157° and melts and decomposes at 166—167°. *Benzenesulphaminomethyl ethyl ketone*, $SO_2Ph{\cdot}NH{\cdot}CH_2{\cdot}COEt$, prepared by interaction with benzenesulphonic chloride, forms colourless, rhombic plates, which sinter at 84° and melt at 88—89°. On treatment in cold aqueous solution with potassium hydroxide and mercuric chloride, the *mercury* salt of 2:5-*diethylpyrazine*, $C_8H_{12}N_2,2HgCl_2$, is formed, decomposing at 168°.

2:5-*Diethylpyrazine*, $\mathrm{CEt}\!<\!\begin{array}{l}\mathrm{CH{:}N}\\ \mathrm{N{\cdot}CH}\end{array}\!\!>\!\mathrm{CEt}$, boils at 185·5—186° and solidifies in a freezing mixture; the *aurichloride* sinters at 155° and decomposes at 156—157°; the *picrate* melts at 93°.

The amino-ketone is reduced by sodium amalgam in acid solution to the α-amino-β-butanol recently described by Tordoir (Abstr., 1902, i, 265), boiling at 168·5—170°; of the derivatives described, the N-*phenylbutylene-ψ-thiocarbamide* [2-*phenylimino-5-ethyltetrahydrothiazole*], melting at 89—90°, is new. With hydrogen bromide, Bookman's (Abstr., 1895, i, 199) β-bromobutylamine is obtained; this sinters at 131°, melts at about 142°, and forms a picrate melting at 140° and decomposing at 213°, not at 150° as given by Bookman.

Phenylaminomethylcarbinol is produced among other products on reducing *iso*nitrosoacetophenone with sodium amalgam in acid solution, and has been characterised by the following salts; the *picrate* crystallises in prismatic plates melting at 146—147° and decomposing at 205°; the *platinichloride* darkens at about 200° and is not melted at 260°, whilst the *benzoyl* derivative forms characteristic colourless plates, which sinter at 143° and melt at 144—145·5°. α-*Hydroxy*-α-

phenyl ethyl phenylthiocarbamide, $NHPh\cdot CS\cdot NH\cdot CH_2\cdot CHPh\cdot OH$, crystallises in needles melting at 131—132°; N-*phenyl phenethylene-ψ-thiocarbamide* [2-*phenylimino*-5-*phenyltetrahydrothiazole*],

$$NPh:C<\begin{matrix} S\text{---}CHPh \\ NH\cdot CH_2 \end{matrix},$$

crystallises in plates or stars melting at 113—115° and forms a picrate melting at 164—165°.

4-*Hydroxy*-3-*propionyl*iso*carbostyril*, $C_6H_4<\begin{matrix} CO\text{------}NH \\ C(OH):C\cdot COEt \end{matrix}$, prepared by heating phthalimidomethyl ethyl ketone with sodium in methyl alcohol, crystallises in needles melting at 231—232° and forms a *phenylhydrazone*, $(C_{12}H_{11}NO_2):N_2HPh$, melting and decomposing at 212—213°. E. F. A.

Halogenated Nitro-derivatives of Benzophenone. FORTUNATO CONSONNO (*Gazzetta*, 1904, 34, i, 374—387).—4 : 4′-*Dichloro*-3 : 3′-*dinitrobenzophenone*, $C_{13}H_6O_4N_2Cl_2$, prepared by the action of fuming nitric acid on *p*-dichlorobenzophenone, separates from acetic acid in small crystals melting at 120° and soluble in alcohol, ether, sulphuric acid, or benzene.

4 : 4′-*Dichloro*-3 : 3′ : 5-*trinitrobenzophenone*, $C_{13}H_5O_6N_3Cl_2$, obtained by the action of potassium nitrate on a sulphuric acid solution of *p*-dichlorobenzophenone, is deposited from acetic acid in crystals melting at 140° and dissolves in sodium hydroxide solution yielding a phenol.

3 : 3′-*Dinitro*-4 : 4′-*dianilinobenzophenone*, $C_{25}H_{18}O_5N_4$, prepared by the interaction of aniline and 4 : 4′-dichloro-5 : 5′-dinitrobenzophenone, separates from acetic acid in orange-yellow crystals melting at 212° and is soluble in alcohol, ether, or benzene, and, with formation of a bright red coloration, in sulphuric acid.

3 : 3′-*Diamino*-4 : 4′-*dianilinobenzophenone*, $C_{25}H_{22}ON_4$, obtained by reducing the preceding compound in alcoholic solution by means of stannous chloride, is deposited from ether in yellow crystals melting at 160°, and dissolves in alcohol or benzene and in sulphuric acid with formation of a red coloration. Its *hydrochloride* forms green crystals melting at 270°.

Diphenyldiphenanthraphenazone ketone,

$$CO\left(C_6H_4<\begin{matrix} NPh(OH)\cdot C\cdot C_6H_4 \\ N\text{---------}C\cdot C_6H_4 \end{matrix}\right)_2,$$

obtained by the action of an acetic acid solution of phenanthraquinone on an alcoholic solution of 3 : 3′-diamino-4 : 4′-dianilinobenzophenone hydrochloride, separates from dilute alcohol in crystals melting at 220° and dissolves in acetic or sulphuric acid. Its *hydrochloride* forms small, yellowish-red crystals soluble in water.

3 : 3′-*Dinitro*-4 : 4′-*diaminobenzophenone*, $C_{13}H_{10}O_5N_4$, prepared by the action of alcoholic ammonia on 4 : 4′-dichloro-5 : 5′-dinitrobenzophenone, forms golden-yellow crystals melting at 121° and dissolves in alcohol, ether, benzene, hydrochloric or sulphuric acid.

3 : 3′ : 4 : 4′-*Tetra aminobenzophenone*, $C_{13}H_{14}ON_3$, obtained by reducing

the preceding compound by means of stannous chloride and hydrochloric acid, crystallises from alcohol in yellow needles melting at 155° and is soluble in ether, benzene, acetic or sulphuric acid.

Diphenanthraphenazine ketone, $CO\left(C_6H_4<\begin{matrix}N\cdot C\cdot C_6H_4 \\ | \quad \| \quad | \\ N\cdot C\cdot C_6H_4\end{matrix}\right)_2$, prepared by the action of an acetic acid solution of phenanthraquinone on the preceding compound, separates from alcohol in brownish-yellow crystals decomposing at 160° and is soluble in acetic acid, and, with formation of a bright red solution, in sulphuric acid.

4 : 4′-*Dichloro*-3 : 3′ : 5 : 5′-*tetranitrobenzophenone*, $C_{13}H_4O_9N_4Cl_2$, obtained by the action of potassium nitrate on a fuming sulphuric acid solution of 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone, is deposited from acetic acid in crystals melting at 202°.

3 : 3′ : 5 : 5′-*Tetranitro*-4 : 4′-*dianilinobenzophenone*, $C_{25}H_{16}O_9N_6$, prepared by the action of aniline on the preceding compound, separates from acetic acid in golden-yellow crystals melting at 262° and is soluble in alcohol, ether, benzene, or sulphuric acid.

3 : 3′ : 5 : 5′-*Tetranitro*-4 : 4′-*dihydroxybenzophenone*, $C_{13}H_6O_{11}N_4$, obtained by the interaction of 4 : 4′-dichloro-3 : 3′ : 5 : 5′-tetranitrobenzophenone, alcohol, and aqueous sodium carbonate, is deposited from alcohol in yellow crystals melting at 203° and is soluble in water, ether, acetic or sulphuric acid.

3 : 3′ : 5 : 5′-*Tetranitro*-4 : 4′-*diaminobenzophenone*, $C_{13}H_8O_9N_6$, prepared by the action of alcoholic ammonia on 3 : 3′ : 5 : 5′-tetranitro-4 : 4′-dichlorobenzophenone, forms yellow crystals melting at 270° and is soluble in alcohol, benzene, acetic or sulphuric acid.

3 : 3′ : 5 : 5′-*Tetranitrotetramethyl*-4 : 4′-*diaminobenzophenone*,

$$C_{17}H_{16}O_9N_6,$$

obtained by the action of dimethylamine on an alcoholic solution of tetranitrobenzophenone (melting at 202°), forms yellow crystals melting at 234°.

3 : 3′-*Dinitro*-4 : 4′-*dimethoxybenzophenone*, $C_{15}H_{12}O_7N_2$, prepared by the action of sodium methoxide on 4 : 4′-dichloro-5 : 5′-dinitrobenzophenone, separates in yellow crystals melting at 205° and is slightly soluble in alcohol or benzene and more so in sulphuric acid.

3 : 3′-*Dinitro*-4 : 4′-*diethoxybenzophenone*, $C_{17}H_{16}O_7N_2$, separates from acetic acid or alcohol in crystals melting at 132°.

3 : 3′-*Dinitro*-4 : 4′-*dihydroxybenzophenone*, $C_{13}H_8O_7N_2$, prepared by the action of potassium hydroxide on either of the two preceding compounds or by the action of aqueous sodium carbonate and alcohol on 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone, is deposited from alcohol in yellow crystals melting at 172° and dissolves in benzene, in alkalis giving a red, and in sulphuric acid a bright red coloration.

3 : 3′-*Dinitro*-4 : 4′-*dimethylaminobenzophenone*, $C_{15}H_{14}O_5N_4$, obtained by the action of an alcoholic solution of methylamine on 4 : 4′-dichloro-3 : 3′-dinitrobenzophenone, separates from alcohol or acetic acid in yellow crystals melting at 212°.

3 : 3′-*Dinitrotetramethyl*-4 : 4′-*diaminobenzophenone*, $C_{17}H_{18}O_5N_4$, is deposited from acetic acid in yellow crystals melting at 150° and dissolves in alcohol, benzene, or sulphuric acid giving a red solution.

T. H. P.

Homologues of ψ-Ionone Hydrate. PIERRE COULIN (D.R.-P. 150771. Compare Abstr., 1903, i, 837).—The method employed for the preparation of ψ-ionone hydrate may also be applied to its homologues. Thus, methyl-ψ-ionone, prepared by condensing citral with methyl ethyl ketone, yields, with phosphoric acid at a low temperature, *methyl-ψ-ionone hydrate*, having a sp. gr. 0·950 at 20°, boiling at 186—192° under 12·5 mm. pressure and forming an oily *semicarbazone*. The mixture of ketones obtained by condensing citral with methyl ethyl ketone in presence of dilute sodium hydroxide forms a *hydrate* having a sp. gr. 0·956 at 20°, boiling at 185—195° under 13·5 mm. pressure, and forming a crystalline semicarbazone which melts at 193°. Ethyl-ψ-ionone, prepared from citral and methyl propyl ketone, forms a *hydrate* having a sp. gr. 0·950 and boiling at 198—205° under 17·5 mm. pressure. C. H. D.

Synthesis of Dialkylated Dihydroxyquinones. FRITZ FICHTER and ADOLF WILLMANN (*Ber.*, 1904, 37, 2384—2390).—3 : 6-*Dihydroxy*-2 : 5-*diethylquinone*, $CO<\begin{matrix}CEt:C(OH)\\C(OH):CEt\end{matrix}>CO$, obtained as a by-product in the preparation of ethyl ethyloxalacetate by the action of sodium on an ethereal solution of ethyl oxalate and ethyl butyrate, crystallises from alcohol or acetic acid in minute flakes, from benzene in needles, has a yellowish-red colour, gives a bluish-violet solution in sulphuric acid, is very volatile, sublimes at 196° under 15 mm. pressure, and melts at 217—218° when heated in a sealed tube. It dissolves in alkali hydroxides to a violet solution, but is reprecipitated on acidifying. The *diacetate*, $C_{14}H_{16}O_6$, crystallises from alcohol in yellow needles and melts at 130°. The *dibenzoate*, $C_{24}H_{20}O_6$, crystallises from benzene in minute spangles and melts at 201°. Reduction and acetylation gives *tetra-acetoxy*-p-*diethylbenzene*, $C_6Et_2(OAc)_4$, which crystallises from alcohol in colourless, glistening flakes and melts at 213°. Reduction of the diacetate just described gives *tetrahydroxy*-p-*diethylbenzene diacetate*, $C_6Et_2(OH)_2(OAc)_2$, which crystallises from alcohol in colourless needles and melts at 205°. When fused with benzoic anhydride, this gives the *tetrabenzoate*, $C_6Et_2(OBz)_2$, which separates from acetic acid in colourless crystals and melts at 275°.

The lower homologue, dihydroxyxyloquinone,

$$CO<\begin{matrix}C(OH):CMe\\CMe:C(OH)\end{matrix}>CO,$$

was prepared by Arnold (*Diss. Würzburg*, 1888) by a method similar to that described above, and its constitution has been established also by preparing it from xyloquinone. *Dimethyldiaminoxyloquinone*,

$$CO<\begin{matrix}CMe:C(NHMe)\\C(NHMe):CMe\end{matrix}>CO,$$

the intermediate substance prepared by the action of methylamine on xyloquinone, crystallises from benzene or alcohol, melts at 227°, and yields the dihydroxy-compound when hydrolysed by 33 per cent. sulphuric acid.

3 : 6 - *Dihydroxy* - 2 : 5 - *di*iso*propylquinone*, $CO<\begin{matrix}CPr^{\beta}:C(OH)\\C(OH):CPr^{\beta}\end{matrix}>CO$,

crystallises from acetic acid in dark red plates, melts in a sealed tube at 154°, sublimes at 165—168° under 15 mm. pressure, and gives a bluish-violet solution in concentrated sulphuric acid. The *diacetate*, $C_{16}H_{20}O_6$, crystallises from alcohol in yellow needles and melts at 137·5°. *Tetra-acetoxydi*iso*propylbenzene*, $C_6Pr_2^{\beta}(OAc)_4$, prepared by reducing and acetylating the diacetate, crystallises from alcohol in colourless, glistening flakes and melts at 245°. T. M. L.

Yellow Dyes of the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 151384).—Bromoanilinoanthraquinonesulphonic acid, prepared by adding bromine to anilinoanthraquinonesulphonic acid made into a paste with water, condenses with aromatic amines on heating in a closed vessel, forming green dyes. Further sulphonation furnishes dark green sulphonic acids. The halogen derivatives prepared in glacial acetic acid solution do not yield similar condensation products. C. H. D.

New Anthracene Dyes. PAUL FRIEDLÄNDER and GEORG SCHICK (*Zeit. Farb. Text. Ind.*, 1904, 3, 218—221. Compare this vol., i, 69).—When dihydroquinizarin is heated with an excess of *p*-toluidine in presence of boric acid (D.R.-P. 91152), a 1 : 4-*di*-p-*toluidinodihydroanthraquinone*, $C_6H_4{<}{C(OH) \atop C(OH)}{>}C_6H_2(NH{\cdot}C_7H_7)_2$, is formed, which rapidly oxidises to 1 : 4-*di*-p-*toluidinoanthraquinone* (*quinizarin-green*), which crystallises from glacial acetic acid in long, slender, indigo-blue needles and melts at 218°. When dihydroquinizarin is heated with 4—5 times its weight of *p*-toluidine in presence of very little hydrochloric acid, quinizarin-blue (1-*hydroxy*-4-p-*toluidinoanthraquinone*), $C_6H_4{:}(CO)_2{:}C_6H_2(OH){\cdot}NH{\cdot}C_7H_7$, is formed.

Anthraquinone-green GX is probably 1 : 4-*di*-p-*toluidinoanthraquinonedisulphonic acid*,

$$SO_3H{\cdot}C_6H_3{:}(CO)_2{:}C_6H_2(NH{\cdot}C_7H_7){\cdot}NH{\cdot}C_7H_6{\cdot}SO_3H$$

$[NH{\cdot}C_7H_7 : NH{\cdot}C_7H_6{\cdot}SO_3H : SO_3H = 1 : 4 : 7]$; on reduction with stannous chloride and hydrochloric acid, it gives *p*-toluidine, *p*-toluidinesulphonic acid, and *dihydroquinizarin*-6(?)-*sulphonic acid*, which is isolated in the form of its barium salt. Anthraquinone-green GX may be obtained by methods which confirm this view. 1-Nitroanthraquinone-6-sulphonic acid is converted by *p*-toluidinesulphonic acid at 200° into 1-sulpho-*p*-toluidinoanthraquinone-6-sulphonic acid,

$$SO_3H{\cdot}C_6H_3{:}(CO)_2{:}C_6H_3{\cdot}NH{\cdot}C_7H_6{\cdot}SO_3H\ ;$$

this, on bromination, gives a 4-bromo-derivative, the bromine atom of which is replaceable by the *p*-toluidino-radicle to form anthraquinone-green GX (D.R.-P. 137566, 138166, 138542).

Alizarin-pure-blue is 2-*bromo*-1-*amino*-4-*sulpho*-p-*toluidinoanthraquinone*, $C_6H_4{:}(CO)_2{:}C_6HBr(NH_2){\cdot}NH{\cdot}C_6H_3Me{\cdot}SO_3H$; on reduction with stannous chloride, it gives hydroquinizarin and *p*-toluidinesulphonic acid, the bromine atom being eliminated. The dye can be obtained by converting α-aminoanthraquinone by the direct action of bromine vapour into its 2 : 4-*dibromo*-derivative, which melts at 221°, and condensing the product with *p*-toluidine; a 2-*bromo*-1-*amino*-4-p-*toluidinoanthraquinone* is obtained, which crystallises from glacial acetic acid

or benzene in long needles, melts at 212°, and on sulphonation gives alizarin-pure-blue.

It appears that it is only the 1 : 4-diaminoanthraquinone dyes that are converted, on reduction by stannous chloride, into the corresponding 1 : 4-dihydroxy-derivatives; 1 : 5-di-*p*-toluidinoanthraquinone on reduction gives merely 1 : 5-*di*-p-*toluidinodihydroanthraquinone*,

$$C_6H_4Me\cdot NH\cdot C_6H_3<\begin{matrix}C(OH)\\ | \\ C(OH)\end{matrix}>C_6H_3\cdot NH\cdot C_6H_4Me,$$

which crystallises from xylene in brownish-yellow needles and melts at 207°. W. A. D.

Action of Formaldehyde on Menthol. EDGAR WEDEKIND and KARL GREIMER (*Zeit. angew. Chem.*, 1904, **17**, 705—711).—The only mentholformaldehyde compounds which are definitely characterised are dimenthyl methylene ether, melting at 57°, and menthyl chloromethyl ether, boiling at 160—162° under 16 mm. pressure, although various other substances are described in the literature as belonging to this class.

The product described as a mentholformaldehyde compound of the type $C_{10}H_{19}\cdot O\cdot CH_2\cdot OH$, and obtained by boiling menthol with an aqueous solution of formaldehyde and dilute hydrochloric acid (D.R.-P. 7278, iv/120), is shown to be a mixture of 2—3 per cent. of menthyl chloride, 3—6 per cent. of menthyl chloromethyl ether, 31—44 per cent. of menthol, and 51—60 per cent. of dimenthyl methylene ether. It is improbable in any case that a menthyl hydroxymethyl ether, $C_{10}H_{19}\cdot O\cdot CH_2\cdot OH$, is stable, since it would most likely be decomposed by the action of water to form menthol and formaldehyde. Attempts to produce it from menthyl chloromethyl ether and silver oxide were accordingly unsuccessful. A. McK.

Preparation of Solid Camphene. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 149791.)—Solid camphene, free from chlorine, is obtained on heating pinene hydrochloride, hydrobromide, or hydriodide with alcoholic ammonia at 220°. Gaseous or aqueous ammonia may also be employed. When alcohol is used, a small quantity of *iso*bornyl ethyl ether is simultaneously formed. C. H. D.

Chemistry of Caoutchouc and its Distillation Products. RUDOLF DITMAR (*Ber.*, 1904, **37**, 2430—2434).—The crude oil resulting from the dry distillation of caoutchouc was submitted to fractional distillation. The behaviour of the various fractions boiling at 35—70°, 70—150°, 150—200°, 200—300°, and more than 300° respectively, towards concentrated nitric acid was different. The first four fractions yielded resins, whilst the fifth yielded a monobasic dinitro-acid, which was also isolated in small amount from both the third and fourth fractions. The nitric acid reaction for caoutchouc is also characteristic for sesqui-, di- and poly-terpenes. A. McK.

Acid Number of Colophony. KARL DIETERICH (*Arch. Pharm.*, 1904, **242**, 255).—Polemical. A reply to Tschirch (*ibid.*, 106, footnote). C. F. B.

Preparation of Benzoylarbutin. CARL VILMAR (D.R.-P. 151036).—When arbutin is benzoylated according to the general method for glucosides, employing an excess of benzoyl chloride, pentabenzoylarbutin is obtained. The monobenzoyl derivative, however, may be prepared by adding benzoyl chloride slowly to an aqueous solution of arbutin, the latter always being in excess, and neutralising from time to time. *Benzoylarbutin* is precipitated, and after crystallisation from hot water forms slender needles and melts at 184·5°. It dissolves in 1800 parts of water at 9°, in 1300 parts at 15°, and in 80 parts at 100°, is almost tasteless, and is readily hydrolysed by alkalis or magnesia. C. H. D.

Rhamnosides. ERNST SCHMIDT (*Arch. Pharm.*, 1904, **242**, 210—224).—This rhamnoglucoside is possibly identical with globulariacitrin from *Globularia alypum* (R. Tiemann, Abstr., 1903, ii, 608).

[With H. BRAUNS.]—Sophorin and caper-rutin from the flower-buds of *Sophora japonica* and *Capparis spinosa* respectively (compare Wachs, Abstr., 1894, i, 299) are shown to be identical with rutin (from *Ruta graveolens*).

[With N. WALIASCHKO.]—Robinin, from the flowers of *Robinia pseudacacia* (Perkin, Trans., 1902, **81**, 473), loses 15·4 per cent. of its weight when dried in a desiccator or in the steam-oven, and then has the composition $C_{33}H_{40}O_{19},\frac{1}{2}H_2O$; its hydrolysis to robigenin, rhamnose, and galactose is expressed by the equation: $C_{33}H_{40}O_{19} + 3H_2O = C_{15}H_{10}O_6 + 2C_6H_{12}O_5 + C_6H_{12}O_6$. Robigenin, $C_{15}H_{10}O_6,H_2O$, is yellow and melts at 268—270°; it forms a colourless *tetra-acetyl* derivative melting at 182—183°; possibly it is identical with the rhamnolutin from the berries of *Rhamnus cathartica* (Tschirch and Polacco, Abstr., 1900, i, 681). In the mother liquor from the crude robinin, lævorotatory asparagine was found in considerable quantity. C. F. B.

Blue Sulphur Dyes. LEOPOLD CASSELLA & CO. (D.R.-P. 150553). —Brilliant blue dyes are obtained by fusing 4-phenylamino-4′-hydroxydiphenylamine or 4-phenylaminophenyl-4′-hydroxytolylamine with sodium sulphide and sulphur. The products form dark blue powders, insoluble in water, but dissolving in solutions of alkali sulphides, and differ from the corresponding dyes from alkylated aminohydroxydiarylamines in their greater fastness towards light. C. H. D.

Optical Isomerides of β-Dihydrofuran-2:5-dicarboxylic Acids. HENRY B. HILL and F. W. RUSSE (*Ber.*, 1904, **37**, 2538—2540. Compare Hill and Wheeler, Abstr., 1901, i, 556).—β-Dihydrofuran-2:5-dicarboxylic acid can be resolved into its optical antipodes by separating the *l*-acid in the form of its sparingly soluble cinchonine salt and the *d*-acid in the form of its strychnine salt. The *d*-acid has $[\alpha]_D + 480·7°$ with $c = 10·15$; $+485·4°$ with $c = 5·08$; $+489·2°$ with $c = 2·525$; $+502°$ with $c = 0·629$; $+519°$ with $c = 0·157$. The *l*-acid has $[\alpha]_D - 478·7°$ with $c = 10·04$; $-483·4°$ with $c = 5·01$; $-488·3°$ with

$c = 2{\cdot}517$; $-507°$ with $c = 0{\cdot}627$; $-533°$ with $c = 0{\cdot}158$. Both acids crystallise with $1H_2O$ and melt when anhydrous at 144°; the *barium* salts crystallise with $1\frac{1}{2}H_2O$, the *lead* salts with $2H_2O$. W. A. D.

9-Diphenylxanthen. FRITZ ULLMANN and GADIENT ENGI (*Ber.*, 1904, 37, 2367—2374).—Methyl *o*-phenoxybenzoate boils at 312° and not at 360° (Arbenz, Abstr., 1890, 892). *o-Phenoxytriphenyl carbinol*, $OPh{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, prepared from it by Grignard's method, crystallises from light petroleum in long, white, silky needles and melts at 120°.

9-*Diphenylxanthen*, $O{<}^{C_6H_4}_{C_6H_4}{>}CPh_2$, prepared by the action of a mixture of sulphuric and acetic acids on the preceding compound, crystallises from hot acetic acid, melts at 200°, has no basic properties, and does not dissolve in strong acids.

9-*Phenylxanthydrol*, $O{<}^{C_6H_4}_{C_6H_4}{>}CPh{\cdot}OH$, prepared from xanthone by Grignard's method, crystallises from benzene in large, glistening, transparent prisms, melts at 158°, and dissolves in strong acids giving yellow, fluorescent solutions which probably contain the oxonium salts. 9-*Phenylxanthen*, $O{<}^{C_6H_4}_{C_6H_4}{>}CHPh$, prepared by reducing with zinc and acetic acid, crystallises from alcohol in large, pointed, pearly crystals and melts at 145°.

4′-*Amino-9-diphenylxanthen*, $O{<}^{C_6H_4}_{C_6H_4}{>}CPh{\cdot}C_6H_4{\cdot}NH_2$, was prepared by heating phenylxanthydrol with aniline hydrochloride and acetic acid; the *hydrochloride* forms long, silky, asbestos-like needles, darkens at 260°, and melts and decomposes at 262—263°; the *base* separates from alcohol in large, glistening, colourless crystals and melts at 227·5°; the diazo-compound is converted by the action of cuprous oxide into diphenylxanthen. 4′-*Dimethylamino-9-diphenylxanthen*, $O{<}^{C_6H_4}_{C_6H_4}{>}CPh{\cdot}C_6H_4{\cdot}NMe_2$, crystallises from acetic acid in glistening, colourless crystals and melts at 195·5°. T. M. L.

A Second Synthesis of Luteolin. S. FAINBERG and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, 37, 2625—2627. Compare Abstr., 1899, i, 370, and this vol., i, 517).—5 : 7 : 3′ : 4′-Tetramethoxyflavanone reacts with bromine in chloroform solution to form 3 : 6 : 8-*tribromo-5 : 7 : 3′ : 4′-tetramethoxyflavanone*, $C_6Br_2(OMe)_2{<}^{O-CH{\cdot}C_6H_3(OMe)_2}_{CO{\cdot}CHBr}$, which crystallises from a mixture of benzene and alcohol in white needles and melts and decomposes at 200°. On addition of hot alcohol and potassium hydroxide to its solution in benzene, white needles of 6 : 8-*dibromo-5 : 7 : 3′ : 4′-tetramethoxyflavone*, $C_6Br_2(OMe)_2{<}^{O-C{\cdot}C_6H_3(OMe)_2}_{CO{\cdot}CH}$, melting at 261—262°, are precipitated. The finely-powdered compound is boiled for 4—5 hours with concentrated hydriodic acid, poured into a solution of sodium hydrogen sulphite, and the product

acetylated. The tetra-acetyl-luteolin thus obtained is hydrolysed by boiling with hydriodic acid, poured into sodium hydrogen sulphite, and recrystallised from dilute alcohol. The luteolin (5 : 7 : 3′ : 4′-tetrahydroxyflavone) thus obtained is identical with that prepared synthetically by Kostanecki, Różycki, and Tambor (Abstr., 1901, i, 92). C. H. D.

7 : 8 : 2′-Trihydroxyflavonol. S. S. Cohen and Stanislaus von Kostanecki (*Ber.*, 1904, 37, 2627—2631).—Salicylaldehyde methyl ether and gallacetophenone dimethyl ether condense together in warm alcoholic solution in presence of sodium hydroxide, forming *2′-hydroxy-3′ : 4′ : 2-trimethoxychalkone*,

$$OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe,$$

crystallising from alcohol in bright yellow needles melting at 105°, and dissolving in concentrated sulphuric acid to an orange-red solution. The *acetyl* derivative forms white needles and melts at 88°.

When the condensation is carried out at the boiling temperature, the chalkone obtained is mixed with the sparingly soluble *7 : 8 : 2′-trimethoxyflavanone*, $C_6H_2(OMe)_2{<}\begin{array}{l}O{-}CH{\cdot}C_6H_4{\cdot}OMe\\ CO{\cdot}CH_2\end{array}$, which crystallises from alcohol in large, colourless prisms, melts at 112°, and dissolves in concentrated sulphuric acid or alcoholic potassium hydroxide to orange-red solutions. The chalkone may also be converted into the flavanone derivative by heating with dilute hydrochloric acid.

iso*Nitroso-7 : 8 : 2′-trimethoxyflavanone*, $C_{18}H_{17}O_6N$, from the flavanone, amyl nitrite, and hydrochloric acid, crystallises from alcohol in thick, yellow tablets and melts and decomposes at 170°. When dissolved in acetic acid and boiled with dilute sulphuric acid, it forms *7 : 8 : 2′-trimethoxyflavonol*, crystallising from alcohol in white needles and melting at 212—214°. It forms a yellow *sodium* salt, and dissolves in sulphuric acid to a greenish-yellow solution. It produces only a faint yellow shade with aluminium mordants. The *acetyl* derivative forms white needles and melts at 138—139°.

Concentrated hydriodic acid converts the trimethoxyflavonol into *7 : 8 : 2′-trihydroxyflavonol*, $C_6H_2(OH)_2{<}\begin{array}{l}O{-}C{\cdot}C_6H_4{\cdot}OH\\ CO{\cdot}C{\cdot}OH\end{array}$, which crystallises from very dilute alcohol in pale yellow needles, melts and decomposes at 298°, and dissolves in dilute sodium hydroxide to a reddish-yellow solution. In accordance with its constitution, it yields brilliant orange shades with aluminium mordants and brown or black shades with iron mordants (compare Katschalowsky and Kostanecki, this vol., i, 608). C. H. D.

7 : 8 : 3′-Trihydroxyflavonol. Stanislaus von Kostanecki and O. Schleifenbaum (*Ber.*, 1904, 37, 2631—2633. Compare preceding abstract).—*2′-Hydroxy-3′ : 4′ : 3-trimethoxychalkone*,

$$OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe,$$

prepared by the condensation of *m*-methoxybenzaldehyde with gallacetophenone dimethyl ether, crystallises from alcohol in yellow

needles and melts at 127—128°. The *acetyl* derivative forms pale yellow needles and melts at 80—81°.

7 : 8 : 3′-*Trimethoxyflavanone*, $C_{18}H_{18}O_5$, forms white needles and melts at 79°. Its iso*nitroso*-derivative crystallises from alcohol in broad, pale yellow needles and melts and decomposes at 168°. It yields a brownish-yellow shade with cobalt mordants.

7 : 8 : 3′-*Trimethoxyflavonol*, $C_{18}H_{16}O_6$, forms pale yellow needles and melts at 188—189°. It forms a yellow sodium salt and produces a pale yellow shade with aluminium mordants. The *acetyl* derivative forms slender, white needles and melts at 165°.

7 : 8 : 3′-*Trihydroxyflavonol*, $C_6H_2(OH)_2<\begin{matrix}O—C\cdot C_6H_4\cdot OH \\ CH\cdot C\cdot OH\end{matrix}$, forms pale yellow needles containing water and melts at 260°. It dyes strong orange shades with aluminium mordants, and brown or black shades with iron mordants. The *tetra-acetyl* derivative forms white needles and melts at 166—167°. C. H. D.

Synthesis of Flavanone. STANISLAUS VON KOSTANECKI and W. SZABRAŃSKI (*Ber.*, 1904, 37, 2634—2635).—Flavanone has not hitherto been prepared, the method employed for its attempted synthesis having yielded the isomeric 2′-hydroxychalkone. The latter may, however, be converted into flavanone by the general method devised by Kostanecki and Lampe (this vol., i, 441) of boiling the alcoholic solution with dilute mineral acid.

Flavanone, $C_6H_4<\begin{matrix}O—CHPh \\ CO\cdot CH_2\end{matrix}$, crystallises from dilute alcohol in small, colourless needles having a faint aromatic odour, and melts at 75—76°. Concentrated sulphuric acid dissolves it to a slightly yellow solution, and alcoholic sodium hydroxide to an orange solution.

Bromine in carbon disulphide solution forms a-*bromoflavanone*, which was not isolated in a pure state. Potassium hydroxide converts this into flavone, thus confirming the constitution of flavanone, and also providing a new synthesis of flavone (compare Feuerstein and Kostanecki, Abstr., 1898, i, 583; Kostanecki and Tambor, Abstr., 1900, i, 239). C. H. D.

The Thiophen Reaction with Nitrous-sulphuric Acid. CARL LIEBERMANN and BERNHARD PLEUS (*Ber.*, 1904, 37, 2461—2464).—The failure to obtain the Liebermann thiophen reaction with samples of coke-oven benzene (Schwalbe, this vol., i, 337) is shown to be due to the small quantity of thiophen in such benzene. The reaction with nitrous-sulphuric acid fails when the proportion of thiophen falls below 0·1 per cent., whereas the isatin reaction is obtained with only 0·01 per cent. A quantitative determination by Dimroth's method (Abstr., 1899, i, 428) showed the Ludwigshafen benzene to contain only 0·077 per cent. of thiophen.

Contrary to Bauer's statement (this vol., i, 519), the indophenine reaction is obtained with pure sulphuric acid free from nitrogen (compare Storch, this vol., i, 610).

[With F. MAUTHNER.]—Indophenine forms *indopheninesulphonic acid*,

$C_{12}H_6NOS \cdot SO_3H$, when heated with sulphuric acid, dissolving in pure water to a blue solution and precipitated by acids. It forms a sparingly soluble *barium* salt, $(C_{12}H_6O_4NS_2)_2Ba$. C. H. D.

Some Liquid Alkaloids. FRIEDRICH W. SEMMLER (*Ber.*, 1904, **37**, 2428—2430).—Determinations of the molecular refraction of the base, $C_{10}H_{17}ON$, previously described (this vol., i, 437, 602) led to the conclusion that the substance in question is a saturated keto-imine having no double linking, and not an unsaturated keto-amine with a double linking. The molecular refraction of coniine, nicotine, and sparteine respectively has now been determined in order to test whether this physical method has any practical use as an aid to determining the constitution of the various liquid alkaloids under consideration.

Coniine has the sp. gr. 0·8440 at 20°, n_D 1·4505, and $\mathfrak{M}_D$ 40·51, values in accordance with Brühl's, which agreed with the representation of coniine as a cyclic saturated imine.

Nicotine has the sp. gr. 1·011 at 20°, n_D 1·5270 at 20°, and $\mathfrak{M}_D$ 49·2, values also in agreement with those of Brühl and in agreement with the theoretical figures.

Sparteine has the sp. gr. 1·0199 at 20°, n_D 1·5291, and $\mathfrak{M}_D$ 70·8, whilst the latter value, calculated for the formula $C_{15}H_{26}N_2$ on the assumption that there is no double linking, and that the nitrogen atoms are tertiary, should be 70·8. It is concluded that the sparteine molecule contains four rings (compare Willstätter and Marx, this vol., i, 613). A. McK.

Damascenine. HERBERT POMMEREHNE (*Arch. Pharm.*, 1904, **242**, 295—298. Compare Abstr., 1899, i, 964; 1900, i, 684; 1901, i, 289). —Of the substance that remains when methyl is eliminated from damascenine by the agency of hydriodic acid, the *hydriodide*,

$$C_8H_9O_3N,HI,$$

melting at 198—200°, and the *hydrochloride*, with $\frac{1}{2}H_2O$, melting at 217—218° when dried, were analysed.

Damascenine is transformed by boiling with baryta water into the same acid substance that is formed when alcoholic potash is used; the *barium* salt obtained has the composition $(C_9H_{10}O_3N)_2Ba,C_9H_{11}O_3N$.

When oxidised with barium permanganate at the ordinary temperature, damascenine yields oxalic acid, ammonia, and methylamine. C. F. B.

Alkine Esters. CHININFABRIK BRAUNSCHWEIG; BUCHLER & CO. (D.R.-P. 151189).—Alkines combine with the haloids of organic alkyloxy- or acetoxy-acids. When acid chlorides are employed, they are best prepared by means of thionyl chloride. The products closely resemble the difficultly prepared, unsubstituted alkine esters in their physiological action.

Acetyltropyltropeine, from acetyltropyl chloride and tropine hydrochloride, forms a syrup crystallising slowly and readily hydrolysing to atropine. *Acetyltropyl-lupineine*, from acetyltropyl chloride and lupinine hydrochloride, has similar properties. *Bromohydratropyltropeine*, from bromohydratropyl bromide and tropine hydrobromide, is crystalline

and melts at 180°. m-*Acetoxybenzoyltropeine* forms a colourless oil, yielding a crystalline *platinichloride*. *Opianyl-lupineine* melts at 100°.
C. H. D.

Preparation of Xanthine Derivatives. C. F. BOEHRINGER & SÖHNE (D.R.-P. 151133).—The 8-methyl group may be removed from 8-trichloromethylxanthines (this vol., i, 340) by boiling with water,

$$\begin{matrix} NR\cdot CO\cdot C\cdot NR \\ CO\cdot NR\cdot C-N \end{matrix}\!\!>\!C\cdot CCl_3 + 2H_2O = CO_2 + 3HCl + \begin{matrix} NR\cdot CO\cdot C\cdot NR \\ CO\cdot NR\cdot C-N \end{matrix}\!\!>\!CH.$$

Since 8-methylxanthines may be prepared from uric acid and its homologues (Abstr., 1902, i, 125), this reaction affords a means of synthesising the xanthine group. Thus theobromine is obtained from 8-trichloromethyltheobromine, and theophylline from 8-trichloromethyl-7-chloromethyl-1 : 3-dimethylxanthine by boiling with water, formaldehyde being eliminated in the latter case. Caffeine is obtained from 8-trichloromethylcaffeine by boiling with water or acetic acid or by fusing with dry oxalic acid.
C. H. D.

Syntheses of Derivatives of Quinoline. EDWARD BARTOW and ELMER V. MCCOLLUM (*J. Amer. Chem. Soc.*, 1904, 26, 700—705).—6-Methylquinoline and 8-nitro-6-methylquinoline can be prepared by Knueppel's modification of Skraup's synthesis, in which arsenic oxide is used as the oxidising agent.

The following compounds were prepared by the action of acetaldehyde on an aromatic amine in presence of hydrochloric acid. 8-*Nitro*-2 : 6-*dimethylquinoline*, obtained from *m*-nitro-*p*-toluidine, crystallises from alcohol in orange-coloured needles and melts at 114°; its *hydrochloride* is described. 6-*Chloro-2-methylquinoline*, prepared from *p*-chloroaniline, crystallises in white flakes, which turn yellow on exposure to the air, and melts at 91°; its *hydrochloride* was obtained as a white powder. 5-(or 7-)-*Chloro-2-methylquinoline*, obtained from *m*-chloroaniline, is a crystalline substance which melts at 78°. 8-*Chloro-2-methylquinoline*, prepared from *o*-chloroaniline, forms white crystals and melts at 64°; this compound may also be obtained by the action of glycol on *o*-chloroaniline in presence of arsenic oxide. 6-*Bromo-2-methylquinoline*, prepared from *p*-bromoaniline, is readily volatile with steam and crystallises from the distillate, melts at 96—97°, and darkens on exposure to the air.
E. G.

Polyhydroxyanthraquinonequinolines. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 149781).—1-Aminoanthraquinone-5- or -8-sulphonic acid may be heated with lime under pressure, forming the corresponding aminohydroxyanthraquinones, which may be converted into quinoline derivatives by heating with glycerol, sulphuric acid, and nitrobenzene or picric acid. The 1 : 5-derivative is a greyish-yellow powder, dissolving in organic solvents to yellow solutions and forming a red sodium salt. Fuming sulphuric acid converts it into a *sulphonic acid*, which yields a *polyhydroxyanthraquinonequinoline* on heating with lime under pressure. This is a sparingly

soluble, dark brown powder, forming blue or violet salts with alkalis. The 1 : 8-derivatives have similar properties. C. H. D.

Immedial-Pure-Blue. ROBERT GNEHM and FELIX KAUFLER (*Ber.*, 1904, 37, 2617—2623).—The substance prepared by melting *p*-dimethylamino-*p*-hydroxydiphenylamine with sulphur and sodium sulphide was oxidised with potassium bromate and hydrogen bromide to a *compound*, $C_{14}H_8ON_2SBr_4$, which was crystallised from nitrobenzene, gave a normal molecular weight in this solvent, and appears to contain two methyl groups. The formula

$$\begin{array}{l} \quad\;\; CBr{:}CH{\cdot}C{\cdot}N{:}C{\cdot}CH{=}CBr \\ \quad\;\;\; | \qquad\quad\; \| \quad\;\; | \qquad\quad\;\; | \\ NMe_2{\cdot}C{:}CBr{-}{-}C{-}S{-}C{:}CBr{\cdot}CO \end{array}$$

is suggested, and this is in accord with the behaviour of the product towards acetic anhydride and towards reducing agents, but it could not be prepared by the action of bromine on methylene-violet.

When the blue was heated in a sealed tube for 4 hours at 130° with sodium chlorate and hydrochloric acid, it was oxidised to tetrachloroquinone, of which a 20 per cent. yield was obtained. T. M. L.

Reactions in the Triphenylmethane Series. EDUARD VONGERICHTEN and K. WEILINGER (*Zeit. Farb. Text. Ind.*, 1904, 3, 217—218. Compare Vongerichten and Bock, Abstr., 1903, i, 721).—*p*-Diaminotriphenylmethane, when heated with *o*-toluidine and *o*-toluidine hydrochloride for 5 hours at 170°, is converted into *p*-diaminophenyldi-*o*-tolylmethane, which melts at 121—122° and gives a *diacetyl* derivative crystallising from alcohol in nodular aggregates and melting at 265—266°; the *tetra-acetyl* derivative, $C_{29}H_{30}O_4N_2$, crystallises from alcohol, melts at 165—166°, and is hydrolysed by alcoholic sodium methoxide to the diacetyl derivative.

On heating *p*-diaminophenyldi-*o*-tolylmethane with an excess of aniline and aniline hydrochloride, it is reconverted into *p*-diaminotriphenylmethane, which melts at 136—137°; its *diacetyl* derivative crystallises from benzene with $1C_6H_6$ and melts at 234—235°; the *tetra-acetyl* derivative, $C_{27}H_{26}O_4N_2$, melts at 172—173°. W. A. D.

Basic Diphenylmethane and Triphenylmethane Dyes. II. Some Derivatives of *para*-Diaminodiphenylmethane. JULIUS VON BRAUN and E. KAYSER (*Ber.*, 1904, 37, 2670—2678; see this vol., i, 344).—*Dicyanodimethyldiaminodiphenylmethane*,

$$CH_2(C_6H_4{\cdot}NMe{\cdot}CN)_2,$$

is formed when cyanogen bromide is slowly added to partially fused tetramethyldiaminodiphenylmethane. It separates from glacial acetic acid as a white, glistening, crystalline powder, melts at 155°, is readily soluble in hot alcohol, but is insoluble in ether or acids. It is oxidised by chromic acid in glacial acetic acid solution to *dicyanodimethyldiaminobenzophenone*, $CO(C_6H_4{\cdot}NMe{\cdot}CN)_2$, which is a white, crystalline substance, melts at 236°, and is soluble only in glacial acetic acid. The *oxime*, $OH{\cdot}N{:}C(C_6H_4{\cdot}NMe{\cdot}CN)_2$, melts at 173°. The ketone does not react with tertiary bases in presence of phosphorus oxychloride, nor with magnesium phenyl bromide.

s-Dimethyldiaminodiphenylmethane is formed when the dicyano-compound is boiled for some hours with dilute hydrochloric or sulphuric acids, or is dissolved in boiling concentrated hydrochloric acid and gradually diluted with water. The *nitroso*-compound,

$$CH_2(C_6H_4{\cdot}NMe{\cdot}NO)_2,$$

melts at 97—98°; the *phenylcarbamide* derivative,

$$CH_2(C_6H_4{\cdot}NMe{\cdot}CO{\cdot}NHPh)_2,$$

melts at 186—187°; the *phenylthiocarbamide* derivative melts at 153°. The action of methyl iodide on dimethyldiaminodiphenylmethane leads to the formation of tetramethyldiaminodiphenylmethane. With benzyl chloride, the *s*-dimethyl base yields *dibenzyldimethyldiaminodiphenylmethane*, $CH_2(C_6H_4{\cdot}NMe{\cdot}CH_2Ph)_2$, which melts at 50°, dissolves in organic solvents or in dilute acids to slightly blue solutions, and forms a *picrate* which melts at 93°.

s-*Dimethyldiaminobenzophenone*, $CO(C_6H_4{\cdot}NHMe)_2$, is obtained by hydrolysing dicyanodimethyldiaminobenzophenone with boiling hydrochloric acid. It melts at 130°, and dissolves readily in alcohol, benzene, chloroform, or dilute acids to yellow solutions. The *platinichloride* crystallises in prisms. The action of cyanogen bromide leads to the re-formation of the colourless dicyano-compound. The *nitroso*-compound, $CO(C_6H_4{\cdot}NMe{\cdot}NO)_2$, melts at 228—229°; the *benzoyl* derivative forms small, white crystals and melts at 204°. G. Y.

Formation of Trialkylated Amidines. JULIUS VON BRAUN (*Ber.*, 1904, **37**, 2678—2685).—The action of phosphorus pentachloride on dialkylated amides in chloroform solution leads to the formation of phosphorus oxychloride and the amide chloride, which is precipitated as a crystalline mass on addition of ether or petroleum of low boiling point, or when the chloroform solution is strongly cooled. These amide chlorides may be boiled in chloroform solution or recrystallised from petroleum of low boiling point without decomposition. With water, the amide chlorides react energetically, re-forming the dialkylated amide; with primary amines, trialkylated amidines are formed. The following compounds have been prepared by this method. Dimethylbenzamide chloride, which melts at 36°; phenyldimethylbenzamidine, from dimethylbenzamide; phenylbenzylmethylbenzamidine, from phenylmethylbenzamide, which boils at 331—332°. *Methyl anthranilate dimethylbenzamidine*, $NMe_2{\cdot}CPh{:}N{\cdot}C_6H_4{\cdot}CO_2Me$, from dimethylbenzamide, phosphorus pentachloride, and methyl anthranilate, forms glistening crystals and melts at 109°; the *picrate*, $C_{17}H_{18}O_2N_2,C_6H_3O_7N_3$, melts at 111—112°; the *platinichloride* is obtained as an orange precipitate. *Phenyldiethylbenzamidine*, from diethylbenzamide, is an oil which boils at 188—189° under 10 mm. pressure; the *picrate* melts at 114°; the *platinichloride* crystallises in glistening, red needles and melts at 206°. Contrary to Claus' statement (*Ber.*, 1882, **15**, 1285), diphenylbenzamide reacts with phosphorus pentachloride in chloroform solution and forms *diphenylbenzamide chloride*, which reacts with aniline to form triphenylbenzamidine; this is a yellow, crystalline powder, melts at 170°, and has slight basic properties. Diphenylbenzamide chloride and *o*-anisidine form

diphenyl-o-anisylbenzamidine, $NPh_2 \cdot CPh\colon N \cdot C_6H_4 \cdot OMe$, which forms a *picrate* melting at 202—203°.

Piperidylphenylbenzamidine, $NPh\colon CPh \cdot C_5NH_{10}$, formed by the action of phosphorus pentachloride and aniline on benzoylpiperidine, or by the action of piperidine on benzanilideimide chloride, is an oil. The *picrate* melts at 174—175°; the *platinichloride* crystallises in red needles and melts at 203°.

p-*Phenetyldimethyl-α-naphthamidine*, $NMe_2 \cdot C(C_{10}H_7)\colon N \cdot C_6H_4 \cdot OEt$, prepared by acting with phosphorus pentachloride and phenetidine on dimethyl-α-naphthoamide, crystallises in white masses, melts at 150°, and is only slightly soluble in organic solvents. The *platinichloride* forms red, matted needles and melts at 220°.

Dimethyl-α-naphthoamide, formed by the action of α-naphthoic chloride on dimethylamine, melts at 62° and boils at 207—208° under 15 mm. pressure. G. Y.

Phenylhydrazino-oxalic Hydrazide and its Derivatives. CARL BÜLOW (*Ber.*, 1904, **37**, 2424—2428).—The monophenylhydrazide of ethyl oxalate, $NHPh \cdot NH \cdot CO \cdot CO_2Et$ (1 mol.), and hydrazine hydrate (1 mol.) yield, in alcoholic solution, *phenylhydrazino-oxalic hydrazide*, $NHPh \cdot NH \cdot CO \cdot CO \cdot NH \cdot NH_2$, which separates in glistening needles and melts at 205—206°. It is soluble in cold dilute hydrochloric acid and more so in dilute aqueous potassium hydroxide. It shows marked amphoteric characteristics and may possibly have the constitution $NHPh \cdot N\colon C(OH) \cdot C(OH)\colon N \cdot NH_2$; it reduces both Fehling's solution and silver nitrate. Its *acetyl* derivative melts at 220—221° and is insoluble in dilute hydrochloric acid, but soluble in potassium hydroxide. Phenylhydrazino-oxalic hydrazide condenses with benzaldehyde to form the *hydrazone*, $NHPh \cdot NH \cdot CO \cdot CO \cdot NH \cdot N\colon CHPh$, which crystallises in glassy needles and melts at 249—250°.

Ethyl 1-*phenylhydrazido-oxalamino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, $NHPh \cdot CO \cdot CO \cdot NH \cdot C_4NMe_2(CO_2Et)_2$, prepared by heating a mixture of phenylhydrazino-oxalic hydrazide and ethyl diacetylsuccinate (compare Bülow, Abstr., 1903, i, 196) in glacial acetic acid, separates in needles and melts at 194—195°. It is easily soluble in concentrated hydrochloric acid and in dilute potassium hydroxide solution. Its solution in concentrated sulphuric acid turns magenta-red when ferric chloride is added. A. McK.

Action of Phenylbenzylhydrazine on Sugars. RUDOLF OFNER (*Ber.*, 1904, **37**, 2623—2625).—The osazone obtained by Neuberg (Abstr., 1902, i, 264) by the action of phenylbenzylhydrazine on lævulose, and also, contrary to Neuberg's statement, from phenylbenzylhydrazine and dextrose, is shown to be a mixed phenyl phenylbenzylosazone, $C_{25}H_{28}O_4N_4$. Its production is due to the fact that commercial phenylbenzylhydrazine always contains phenylhydrazine. Pure phenylbenzylhydrazine does not react with dextrose or lævulose, but Neuberg's osazone is precipitated on the addition of phenylhydrazine to the solution. The same osazone is obtained by the action of phenylbenzylhydrazine on phenyldextrosazone. Votoček's statement (*Zeit. Zuckerind. Böhm.*, 1903, **27**, 708) that secondary aromatic hydr-

azines do not react with aldoses, but react with their phenylhydrazones, is therefore correct. C. H. D.

Melting Point of Glycuronic Acid Semicarbazone. G. Giemsa (*Zeit. physiol. Chem.*, 1904, 41, 548. Compare Abstr., 1901, i, 11; and Fromm, this vol., ii, 360).—The author adheres to his previous statement that the semicarbazone of glycuronic acid lactone, when carefully heated, melts and decomposes at 188—189°.

J. J. S.

Ethyl *N*-Amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate as the Parent Substance for the Preparation of *N*-Bispyrrole Derivatives. Carl Bülow and Constantin Sautermeister (*Ber.*, 1904, 37, 2697—2702).—By the action of hydrazine on ethyl $\alpha\beta$-diacetylpropionate, Korschun (this vol., i, 614) has obtained ethyl 3 : 6-dimethyl-4 : 5-dihydropyridazine-4-monocarboxylate, previously described by Bülow (Abstr., 1903, i, 196), and a second product, which gave, on hydrolysis, an acid which is possibly *N*-bis-2 : 5-dimethylpyrrole-3-(or 4)-carboxylic acid.

The authors have studied the formation of *N*-bisethyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, $\begin{matrix} CO_2Et\cdot C{:}CMe \\ CO_2Et\cdot C{:}CMe \end{matrix}\!\!>\!N\cdot N\!<\!\!\begin{matrix} CMe{:}C\cdot CO_2Et \\ CMe{:}C\cdot CO_2Et \end{matrix}$, from Bülow's ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate.

Ethyl diacetylsuccinate reacts with ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate according to the equation :

$$C_4NMe_2(CO_2Et)_2\cdot NH_2 + \begin{matrix} CO_2Et\cdot C{:}CMe\cdot OH \\ CO_2Et\cdot C{:}CMe\cdot OH \end{matrix} = 2H_2O + \begin{matrix} CO_2Et\cdot C{:}CMe \\ CO_2Et\cdot C{:}CMe \end{matrix}\!\!>\!N\cdot N\!<\!\!\begin{matrix} CMe{:}C\cdot CO_2Et \\ CMe{:}C\cdot CO_2Et \end{matrix}.$$

N-*Bisethyl 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate*, thus obtained, separates from alcohol in colourless needles or stellate leaflets and melts at 126—127°. It may also be prepared from ethyl diacetylsuccinate (2 mols.) and hydrazine hydrate (1 mol.).

N-*Bis-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid*, prepared by hydrolysing the preceding ester, crystallises with $1H_2O$ and becomes anhydrous at 80—92°; when quickly heated, the anhydrous acid does not melt or decompose below 290°; when heated for 6—7 hours at 100—120°, it suffers very slight decomposition, carbon dioxide being evolved. It does not give a sharp end-point when titrated with phenolphthalein. A. McK.

Formation of Indazoles from Nitrated *o*-Methylated Amines. Emilio Noelting (*Ber.*, 1904, 37, 2556—2597).—3-*Nitrotolueneazo-7-nitroindazole*, $NO_2\cdot C_6H_3\!<\!\!\begin{matrix} C\text{———}N{:}N\cdot C_6H_3Me\cdot NO_2 \\ N \end{matrix}\!\!>\!NH$, prepared by diazotising nitrotoluidine $[CH_3 : NH_2 : NO_2 = 1 : 2 : 3]$, crystallises from acetic acid in orange-coloured needles and melts at 250—251°. The *7-nitroindazole*, $NO_2\cdot C_6H_3\!<\!\!\begin{matrix} CH \\ N \end{matrix}\!\!>\!NH$, from which it is derived, melts at 186·5—187·5°, is volatile with steam, and readily

sublimes in yellow needles. 7-*Nitro-2-methylindazole*,

$$NO_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NMe,$$

prepared by the action of methyl sulphate on the indazole, crystallises from alcohol in yellow needles, melts at 144—145°, and is very stable towards hydrolysing agents. 7-*Nitro-2-acetylindazole*,

$$NO_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NAc,$$

crystallises from a mixture of benzene and light petroleum in white flakes melting at 131—132°, but, after repeated crystallisation from dilute alcohol, the melting point is raised to 186·5—187·5°; the compound decomposes very readily. 7-*Aminoindazole*,

$$NH_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH,$$

prepared by reducing the nitro-compound with ferrous hydroxide or ammonium sulphide, crystallises from dilute alcohol in silvery-white flakes, melts at 155—156°, and becomes red when exposed to the light.

The *diacetyl* derivative, $NHAc\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NAc$, crystallises from alcohol in needles or prisms, from benzene in plates, and melts at 160·5—161·5°. The p-*nitrobenzylidene* derivative,

$$NO_2\cdot C_6H_4\cdot CH\!:\!N\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH,$$

separates from alcohol in golden-yellow needles and melts at 227—229°.

The *hydrochloride* of 6-nitroindazole (Witt, Noelting, and Grandmougin, Abstr., 1891, 312) melts at 168·5—169·5°, becomes solid again at 173° (liberation of hydrogen chloride and separation of the indazole), and again melts at 178—179° (m. p. of indazole, 181°); it is decomposed by water and by alcohol, and was prepared by the action of hydrogen chloride on a solution of the indazole in benzene. The *platinichloride*, $(C_7H_5O_3N_3)_2,H_2PtCl_6$, forms yellow needles, is decomposed by water, and was therefore prepared from a solution of the indazole in a mixture of acetic anhydride and acetic acid. The *platinichloride* of the methylated indazole, $(C_8H_7O_3N_2)_2,H_2PtCl_6$, is decomposed by water and by alcohol, but was prepared from a 20 per cent. solution of hydrogen chloride, from which it separated in yellow crystals. 2-*Benzyl*-6-*nitroindazole*, $NO_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>N\cdot CH_2Ph$, crystallises from methyl alcohol in long, yellow needles and melts at 111—112°. 2-*Benzoyl*-6-*nitroindazole*, $NO_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NBz$, crystallises from alcohol in white, felted needles, melts at 165—165·5°, and is more stable than the acetyl derivative, although readily hydrolysed by dilute sodium hydroxide. The polymeric *nitrotolueneazo-nitroindazole*, $NO_2\cdot C_6H_3<\overset{C\text{———}N_2\cdot C_6H_3Me\cdot NO_2}{\underset{N}{|}}>NH$, a by-product in the preparation of the indazole, forms brownish-yellow spangles and

decomposes at a high temperature without melting. The diazoamino-compound, $NO_2\cdot C_7H_5\cdot N:N\cdot NH\cdot C_7H_5\cdot NO_2$, is also formed under certain conditions. The *platinichloride*, $C_7H_7N_3,H_2PtCl_6$, of 6-aminoindazole, $NH_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH$ (W. N. & G., *loc. cit*), crystallises in yellow needles. The p-*nitrobenzylidene* derivative,

$$NO_2\cdot C_6H_4\cdot CH:N\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH,$$

crystallises from alcohol and melts at 215—216°. The *dimethyl*-p-*aminobenzylidene* derivative, $NMe_2\cdot C_6H_4\cdot CH:N\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH$, crystallises from benzene in yellow crystals with a blue lustre and melts at 198—199°; it dyes silk and cotton (the latter with tannin mordant) an intense yellow; it is hydrolysed again by long boiling in acid solution. A *double* compound of 6-aminoindazole and *trinitrobenzene*, $C_7H_7N_3,C_6H_3(NO_2)_3$, separates from absolute alcohol in long, ruby-red needles and melts at 153—154°. *Dinitrophenyl*-6-*indazolylamine*, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH$, prepared by the action of chlorodinitrobenzene on the base, crystallises from a mixture of alcohol and benzene in reddish-yellow needles and melts at 161°; it is a weak yellow dye for silk and wool. The *trinitrophenyl* derivative,

$$C_6H_2(NO_2)_3\cdot NH\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH,$$

prepared by the action of picryl chloride on the amine, crystallises from a mixture of alcohol and benzene in orange-coloured needles, begins to decompose at 240°, and becomes liquid between 240° and 250°.

4-*Nitroindazole*, $NO_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH$, crystallises from boiling water in colourless, silky needles, dissolves in alkalis, is only slightly volatile in steam, and melts at 203°. Hydrogen chloride precipitates the *hydrochloride* from benzene in colourless flocks. The *platinichloride*, prepared in the same way as that of 6-nitroindazole, forms yellow needles and resembles its isomeride. 4-*Nitro-2-methylindazole*, $NO_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NMe$, prepared by the action of methyl sulphate on the indazole, crystallises from alkaline water in yellow needles, melts at 81—82°, is readily soluble in alcohol, can be distilled, dissolves in 15 per cent. hydrochloric acid, and is stable towards alkali hydroxides even when heated. The *benzoyl* derivative, $C_{14}H_9O_3N_3$, crystallises in colourless needles and melts at 162—163°.

5-*Nitroindazole*, $NO_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NH$, crystallises in colourless, silky needles, melts at 208°, is sparingly volatile with steam, and dissolves in alkalis. 5-*Nitro-2-methylindazole*, $NO_2\cdot C_6H_3<\overset{CH}{\underset{N}{|}}>NMe$, crystallises from a mixture of benzene and light petroleum in yellow needles, melts at 128—129°, and is soluble in hydrochloric acid of

12 per cent. strength and above. The *platinichloride* forms yellow needles and is decomposed by water and alcohol, but can be crystallised from dilute hydrochloric acid.

5-*Nitro-2-acetylindazole*, $NO_2\cdot C_6H_3{<}\begin{smallmatrix}CH\\|\\N\end{smallmatrix}{>}NAc$, crystallises from acetic anhydride in snow-white needles and melts at 158—159°; the acetyl group is removed by boiling in aqueous alcoholic solution or by potassium hydroxide in the cold. *Chloro-5-aminoindazole*,

$$NH_2\cdot C_6H_2Cl{<}\begin{smallmatrix}CH\\|\\N\end{smallmatrix}{>}NH,$$

prepared by reducing the nitroindazole with stannous chloride and hydrogen chloride (chlorination accompanies reduction), crystallises from boiling water in silky spangles and melts at 172—173°.

7-*Nitro-4-methylindazole*, $NO_2\cdot C_6H_2Me{<}\begin{smallmatrix}CH\\|\\N\end{smallmatrix}{>}NH$, crystallises from alcohol in golden, glistening needles and melts at 180—181°.

6-*Nitro-4-methylindazole* forms yellowish-white needles and melts at 177—178°.

5-*Nitro-4-methylindazole* forms yellowish-white needles, is only sparingly soluble in acetic acid, and melts at 259°.

6-(or 4)-*Nitro-7-methylindazole*; a mixture of the isomerides is obtained, and can be separated by fractional crystallisation from water; the less soluble isomeride melts at 222·5°, the more soluble at 175—176°; the respective constitutions are not determined.

4 : 6-*Dinitro-7-methylindazole*, $C_6HMe(NO_2)_2{<}\begin{smallmatrix}CH\\|\\N\end{smallmatrix}{>}NH$, crystallises from alcohol in long, pale yellow prisms and melts and decomposes at 200°; hydrogen chloride precipitates the hydrochloride from benzene.

6-*Nitro-5-methylindazole* crystallises from water in pale yellow needles and melts at 173—174°. The *acetyl* derivative,

$$NO_2\cdot C_6H_2Me{<}\begin{smallmatrix}CH\\|\\N\end{smallmatrix}{>}NAc,$$

forms colourless needles and melts at 182—183°.

4-*Nitro-5-methylindazole* closely resembles its isomerides and melts at 198—199°.

4 : 6-*Dinitro-5-methylindazole*, $C_6HMe(NO_2)_2{<}\begin{smallmatrix}CH\\|\\N\end{smallmatrix}{>}NH$, crystallises from methyl alcohol in colourless needles and melts at 190—191°.

7-*Nitro-6-methylindazole* separates from alcohol, water, or benzene in minute, yellow needles or flakes, and from methyl alcohol in long, well-formed prisms, melts as low as 162°, is somewhat volatile with steam, and sublimes in long, slender, amber-yellow prisms. 7-*Amino-6-methylindazole* crystallises in snow-white, felted needles and melts and blackens at 194°.

4-*Nitro-6-methylindazole* crystallises from dilute acetic acid in colourless needles and melts at 206—207°.

5-*Nitro-6-methylindazole* melts at 231—232°. The *acetyl* derivative forms colourless needles, melts at 203—204°, and is easily hydrolysed.

p-*Nitroxylenol acetate*, $NO_2\cdot C_6H_2Me_2\cdot OAc$, obtained as a by-product, crystallises from alcohol in pale yellow prisms and melts at 72—73°.

5 : 7-*Dinitro*-6-*methylindazole* crystallises in colourless needles and melts at 229°.

4- or 6-*Nitro*-5 : 7-*dimethylindazole* melts at 180—181°.

4 : 6-*Dinitro*-5 : 7-*dimethylindazole* crystallises from alcohol in yellowish-white needles and melts at 247°.

7-*Nitro*-5 : 6-*dimethylindazole* crystallises from benzene in pale yellow needles and melts at 180·5—181·5°.

4-*Nitro*-5 : 6-*dimethylindazole* crystallises from benzene in white, silvery flakes and melts at 204°.

4 : 7-*Dinitro*-5 : 6-*dimethylindazole* crystallises from anisole in silky, greenish-white needles; the crude product melted at 208°, but no melting point is given for the recrystallised substance. A table is given showing the properties of all the nitrated indazoles, with the bases from which they are derived, and the yields of indazole with four different methods of decomposing the diazo-compound. T. M. L.

Pyrazolones Derived from α-Mono-substituted Acetoacetic Esters. René Locquin (*Bull. Soc. chim.*, 1904, [iii], 31, 760—762. Compare Rothenburg, Abstr., 1895, i, 686, and Bouveault and Locquin, this vol., i, 551).—The following pyrazolones were obtained by the condensation of the appropriate ester with hydrazine hydrate. 3-*Methyl*-4-*propyl*-5-*pyrazolone*, $C_7H_{12}ON_2$, crystallises in slender needles from a mixture of alcohol and light petroleum or from boiling dilute alcohol and melts and sublimes at 212—213° (corr.). 3-*Methyl*-4-iso*butyl*-5-*pyrazolone* forms slender needles, melts at 237° (corr.), is soluble in boiling alcohol or boiling water, slightly so in ether, and insoluble in light petroleum. 3-*Methyl*-4-n-*amyl*-5-*pyrazolone* crystallises in brilliant lamellæ from dilute alcohol or boiling benzene and melts at 186—187° (corr.): the *isomeride* prepared from ethyl *iso*amylacetoacetate crystallises in spangles and melts at 217—218° (corr.). 3-*Methyl*-4-n-*octyl*-5-*pyrazolone* separates from boiling benzene in lamellæ with a metallic lustre, melts at 182° (corr.), and is readily soluble in light petroleum. 3-*Methyl*-4-sec-*octyl*-5-*pyrazolone* crystallises by spontaneous evaporation of its solution in ether, melts at 137° (corr.), and is slightly soluble in light petroleum. T. A. H.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. VIII. Conversion of the s-Dibromobenzoylhydrazines into Derivatives of Furodiazole [Oxadiazole], and Thiodiazole. Robert Stollé and Akop Johannissien (*J. pr. Chem.*, 1904, [ii], 69, 474—481. Compare Abstr., 1903, i, 721; this vol., i, 102, 200, 453).—To prepare the s-dibromobenzoylhydrazines, the acid is treated with phosphorus pentachloride, the product shaken with ice-water to remove hydrogen chloride and phosphorus oxychloride, and the ethereal solution of the acid chloride so obtained shaken with hydrazine sulphate and excess of sodium hydroxide solution.

s-*Di*-o-*bromobenzoylhydrazine* crystallises in white needles and melts at 245°. When heated with phosphoric oxide in a vacuum, it yields *di*-o-*bromophenyloxadiazole*, $\begin{matrix} N{:}C(C_6H_4Br) \\ | \\ N{:}C(C_6H_4Br) \end{matrix}\!>\!O$, which crystallises in

leaflets, melts at 108°, and boils at 240—250° under 13 mm. pressure. When heated with phosphorus pentasulphide at 200° in a vacuum, *s*-di-*o*-bromobenzoylhydrazine yields *di-o-bromophenylthiodiazole*, which crystallises from alcohol and melts at 117°.

s-Di-*m*-bromobenzoylhydrazine (Curtius and Portner, Abstr., 1899, i, 136) yields *di*-m-*bromophenyloxadiazole*, which crystallises in white, microscopic needles and melts at 179°, and *di*-m-*bromophenylthiodiazole*, which crystallises in delicate needles and melts at 175°.

s-*Di*-p-*bromobenzoylhydrazine* crystallises in leaflets and melts and decomposes at about 300°. It forms *di*-p-*bromophenyloxadiazole*, which crystallises in long needles and melts at 249°, and *di*-p-*bromophenylthiodiazole*, which crystallises from alcohol and melts at 237°.

G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. IX. Conversion of the Hydrazines of Propionic and *iso*Valeric Acids into Heterocyclic Compounds. Robert Stollé and Hermann Hille (*J. pr. Chem.*, 1904, [ii], 69, 481—485. Compare Abstr., 1902, i, 141).—*Diethyloxadiazole* is formed when *s*-dipropionylhydrazine is heated with phosphoric oxide or with propionic anhydride at 200° in a sealed tube; it boils at 198° under 760 mm. pressure, is miscible with water, alcohol, or ether, and gives a white precipitation with mercuric chloride.

Diethylthiodiazole, obtained by heating *s*-dipropionylhydrazine with phosphorus pentasulphide under reduced pressure, boils at 105° under 14 mm. pressure and is miscible with water, alcohol, or ether.

*Di*iso*butyl*-s-*dihydrotetrazine*, $C_4H_9\cdot C\lessgtr{}^{NH\cdot N}_{N\cdot NH}\gtrdot C\cdot C_4H_9$, is obtained in the preparation of *iso*valerylhydrazide from hydrazine hydrate and ethyl *iso*valerate (Hille, *loc. cit.*). It crystallises in plates and melts at 197°.

*Di*iso*butyloxadiazole* is obtained when ethyl *iso*valerate is heated with hydrazine hydrate in a sealed tube at 220—230°. It is a strongly refractive, colourless liquid, which boils at 140° under 17 mm. or at 232° under 760 mm. pressure. It is miscible with alcohol, ether, or much water and gives a white precipitation with mercuric chloride.

*Di*iso*butylthiodiazole*, formed by heating s-di*iso*valerylhydrazine with phosphorus pentasulphide, is a colourless liquid. It boils at 130—132° under 25 mm. pressure and is miscible with alcohol or ether, but not with water. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. X. Conversion of the *n*-Butyryl Hydrazides into Heterocyclic Compounds. Robert Stollé and Gustav Zinsser (*J. pr. Chem.*, 1904, [ii], 69, 486—496).—n-*Butyrylhydrazide*, obtained together with a small amount of *s*-di-*n*-butyrylhydrazine when ethyl butyrate is boiled with hydrazine hydrate, crystallises in needles, melts at 44°, boils at 138° under 20 mm. pressure, is very hygroscopic, and reduces ammoniacal silver nitrate in the cold. The *hydrochloride*, $C_3H_7\cdot CO\cdot N_2H_3,HCl$, is obtained as a white, crystalline powder which melts at 148°. *Butyrylbenzylidenehydrazide*,

$$C_3H_7\cdot CO\cdot NH\cdot N:CHPh,$$

crystallises in slender, yellow needles and melts at 98°. n-*Butyrylacetonehydrazide*, $C_3H_7\cdot CO\cdot NH\cdot N\colon CMe_2$, crystallises in glistening leaflets and melts at 82°.

3 : 6-*Dipropyl*-s-*dihydrotetrazine*, $C_3H_7\cdot C\ll^{NH\cdot N}_{N\cdot NH}\gg C\cdot C_3H_7$, is formed when butyrylhydrazide is heated in a sealed tube at 180°; it crystallises in leaflets, melts at 179°, is easily soluble in water, alcohol, or glacial acetic acid, and does not reduce ammoniacal silver solutions on warming.

s-Dibutyrylhydrazine and a small amount of dipropyloxadiazole are formed when hydrazine hydrate is heated with excess of ethyl butyrate in a sealed tube at 150°. *s*-Dibutyrylhydrazine is obtained in better yield by the action of butyric anhydride on hydrazine hydrate.

s-*Di*-n-*butyrylhydrazine* crystallises from alcohol, melts at 168°, boils at 214° under 24 mm. pressure, reduces ammoniacal silver solutions in presence of sodium hydroxide, and forms a *copper* compound, $(C_3H_7\cdot CO)_2N_2Cu$ or $C_3H_7\cdot CO\cdot NH\cdot N(Cu\cdot OH)\cdot CO\cdot C_3H_7$, as a green precipitate on addition of copper acetate to the aqueous solution.

Dipropyloxadiazole, $CPr^{\alpha}\ll^{N\cdot N}_{-O-}\gg CPr^{\alpha}$, is formed when *n*-butyrylhydrazide is heated with excess of *n*-butyric anhydride at 150° under pressure. It is a colourless liquid which boils at 123° under 19 mm., or at 227° under atmospheric pressure, is miscible with water, alcohol, or ether, and forms a white emulsion with mercuric chloride in aqueous solution.

Dipropylthiodiazole, obtained by heating dibutyrylhydrazine with phosphorus pentasulphide, is a yellow liquid which boils at 127° under 13 mm. pressure, is easily soluble in alcohol, ether, or chloroform, and in concentrated aqueous solution gives white precipitates on addition of silver nitrate or mercuric chloride.

2 : 5-*Dipropyl*-1 : 3 : 4-*triazole* is formed when dibutyrylhydrazine is heated with ammonium zinc chloride at 250°, and is also obtained as a by-product from the preparation of dibutyrylhydrazine from ethyl butyrate and hydrazine hydrate, probably owing to intermediate formation of dipropyldihydrotetrazine. Dipropyltriazole melts at 70°, boils at 177° under 16 mm. pressure, is hygroscopic, and forms a *silver* compound, $\genfrac{}{}{0pt}{}{N\colon CPr^{\alpha}}{\overset{|}{N}\colon CPr^{\alpha}}\!\!>NAg$. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XI. Conversion of *iso*Butyric Acid into Heterocyclic Compounds. ROBERT STOLLÉ and LEO GUTMANN (*J. pr. Chem.*, 1904, [ii], 69, 497—502).—iso*Butyrylhydrazide*,

$$NH_2\cdot NH\cdot COPr^{\beta},$$

obtained by boiling ethyl *iso*butyrate with hydrazine hydrate, crystallises in glistening needles, melts at 104°, is easily soluble in alcohol or water, and reduces ammoniacal silver and Fehling's solutions. iso-*Butyrylbenzylidenehydrazide* crystallises in delicate, yellow needles and melts at 103°. iso*Butyrylacetonehydrazide* melts at 90—91°. 3 : 6-*Di*iso-

propyl-s-*dihydrotetrazine*, $CPr^{\beta}<\frac{NH\cdot N}{N\cdot NH}>CPr^{\beta}$, formed when *iso*-butyrylhydrazide is heated at 270° under pressure, crystallises in glistening leaflets and melts and decomposes at 221°.

*Di*iso*butyrylhydrazine*, $COPr^{\beta}\cdot NH\cdot NH\cdot COPr^{\beta}$, formed by the action of *iso*butyric anhydride on hydrazine hydrate in the cold, crystallises in white, matted needles, melts at 239°, and is easily soluble in hot alcohol. *Di*iso*propyloxadiazole*, prepared by the action of *iso*butyric anhydride on di*iso*butyrylhydrazine at 150° under pressure, boils at 209° and gives a white *precipitate* with mercuric chloride in aqueous solution. 2 :5-*Di*iso*propyl*-1 : 3 : 4-*triazole* forms a white, crystalline mass which melts at about 140—150°. With silver nitrate in ammoniacal alcoholic solution, it forms a *silver* compound, $C_8H_{14}N_3Ag$. *Di*iso*propylthiodiazole* is a liquid which boils at 126° under 27 mm. pressure, and forms white precipitates with mercuric chloride or silver nitrate in aqueous solution. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XII. Conversion of *s*-Dilaurylhydrazine into Diazole Derivatives. Robert Stollé and Christian Schätzlein (*J. pr. Chem.*, 1904, [ii], 69, 503—505).—*Diundecyloxadiazole*, $C_{11}H_{23}\cdot C<\frac{N\cdot N}{-O-}>C\cdot C_{11}H_{23}$, obtained by heating *s*-dilaurylhydrazine under reduced pressure, crystallises in feathery aggregates of needles, melts at 56°, boils at 275° under 22 mm. pressure, and is hydrolysed to dilaurylhydrazine when boiled with dilute sulphuric acid. *Diundecylthiodiazole*, formed when dilaurylhydrazine is heated with phosphorus pentasulphide, crystallises in feathery masses and melts at 49°. 2 : 5-Diundecyl-1 : 3 : 4-triazole is formed when laurylhydrazide is heated under pressure at 300°, or when diundecyl-*s*-dihydrotetrazine is heated at 250° in a vacuum. It crystallises in small needles, melts at 89°, and forms a *silver* derivative with silver nitrate in alcoholic solution. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XIII. Dipentadecylfurodiazole and Dipentadecylthiodiazole. Robert Stollé and F. H. Dellschaft (*J. pr. Chem.*, 1904, [ii], 69, 506—508).—*Dipentadecyloxadiazole* is formed along with a *substance* which crystallises in flat, yellow needles and melts at 118°, when *s*-dipalmitylhydrazine is heated under reduced pressure. It separates from alcohol in feathery crystals, melts at 72°, and is hydrolysed by boiling dilute sulphuric acid, but not by dilute alcoholic sodium hydroxide, to *s*-dipalmitylhydrazine.

Dipentadecylthiodiazole, formed along with the substance melting at 118° when *s*-dipalmitylhydrazine is heated with phosphorus pentasulphide, melts at 60°. G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XIV. Selenodiazole. Robert Stollé and Leo Gutmann (*J. pr. Chem.*, 1904, [ii], 69, 509—512).—*Dimethylselenodiazole*, $CMe<\frac{N\cdot N}{-Se-}>CMe$, formed when *s*-diacetylhydrazine is heated

with phosphorus pentaselenide, melts at 77°, boils at 121° under 23 mm. pressure, dissolves in concentrated sulphuric acid to a green solution, and forms an *additive* compound, $C_4H_6N_2Se,AgNO_3$, with silver nitrate in alcoholic solution.

Diphenylselenodiazole, from *s*-dibenzoylhydrazine and phosphorus pentaselenide, crystallises in glistening scales, melts at 156°, is easily soluble in alcohol or ether, and does not react with dilute acids or alkalis, or with ammoniacal silver nitrate. G. Y.

Action of Hydrogen Selenide on Nitriles. W. Becker and Julius Meyer (*Ber.*, 1904, **37**, 2550—2555).—As stated by von Dechend (this Journal, 1875, 270), benzonitrile, in presence of a small quantity of alcoholic ammonia, is readily converted by hydrogen selenide into selenobenzamide, $CSePh{\cdot}NH_2$, which is transformed by iodine in alcoholic solution into *dibenzenylazoselenime* [3 : 5-*diphenyl*-1 : 2 : 4-*selenodiazole*], $CPh\lessgtr\overset{Se\cdot N}{\underset{N\text{———}}{}}\!>CPh$. This substance crystallises in long, white, silky needles, melts at 85°, and gives a *platinichloride*, $(C_{14}H_{10}N_2Se)_2,H_2PtCl_6$, separating in golden-yellow crystals; on reduction with alcoholic sodium, it gives benzylamine, but with zinc and hydrochloric acid the action is different, and a well-defined product could not be isolated. On this account, the substance seems to be similar to the dibenzenylazoximes and dibenzenylazosulphimes, and the alternative formula, $CPh\lessgtr\overset{N\cdot N}{\underset{Se}{}}>CPh$, less probable than that given above.

p-*Toluic selenoamide*, $C_6H_4Me{\cdot}CSe{\cdot}NH_2$, prepared from *p*-toluonitrile and hydrogen selenide, crystallises from alcohol in beautiful, golden needles, melts at 161°, and is converted by iodine into p-*dimethyldibenzenylazoselenime* [3 : 5-*di*-p-*tolyl*-1 : 2 : 4-*selenodiazole*],

$$C_6H_4Me{\cdot}C\lessgtr\overset{Se\cdot N}{\underset{N\text{———}}{}}>C{\cdot}C_6H_4Me,$$

which crystallises from alcohol in white needles, melts at 116°, and gives a *platinichloride*, $(C_{16}H_{14}N_2Se)_2,H_2PtCl_6$. On reduction with alcoholic sodium, it gives *p*-tolylmethylamine, $C_6H_4Me{\cdot}CH_2{\cdot}NH_2$, but with zinc and hydrochloric acid another substance, possibly tolenylamidine, $C_6H_4Me{\cdot}C(NH_2){:}N{\cdot}CH_2{\cdot}C_6H_4Me$, is produced.

Attempts to combine hydrogen selenide with aliphatic nitriles gave no issue. Similarly, experiments to condense thioacetamide, either with itself or with thiobenzamide, were fruitless. Hydrogen selenide does not combine with benzyl cyanide, but simply hydrolyses it to phenylacetic acid. W. A. D.

The Polyacid Salts of Rosaniline. Jules Schmidlin (*Compt. rend.*, 1904, **138**, 1508—1510).—The author has prepared the following triacid salts of the rosaniline series in a state of purity: rosaniline trihydrochloride, black crystals; pararosaniline trihydrochloride, black crystals; hexamethyl pararosaniline trihydrochloride, violet-black powder; all these salts dissolve in water or alcohol with the same colour as the corresponding mono-acid salts. Rosenstiehl described a magenta tetrahydrochloride obtained by saturating the base with

hydrogen chloride and removing the excess of acid by means of a current of air; the author finds that this method does not gives a definite compound, the amount of hydrogen chloride absorbed increasing as the temperature decreases, thus a pentahydrochloride of a red colour is obtained at the ordinary temperature and pressure, but as the temperature is lowered more hydrogen chloride is absorbed and the compound becomes orange, until at $-70°$ the colour is a pale yellow and the composition of the compound is intermediate between a hexa- and a hepta-hydrochloride, whilst at the temperature of liquid air hydrogen chloride is rapidly absorbed and the product is white.

M. A. W.

Transformation of Azo-compounds containing an Ortho-substituted Alcohol Radicle into Indazyl Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1904, 138, 1276—1278).—Benzene-*o*-azobenzyl alcohol on distillation, or when warmed at 100° with dilute sulphuric acid, is converted by loss of H_2O into phenylindazole (compare Abstr., 1903, i, 585). In the cold, and even at 100° in alkaline, neutral, or only feebly acid solution, it is, on the other hand, relatively stable.

The two di-ortho-substituted azo-compounds,

$$OH\cdot CH_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CO_2H$$

and $N_2(C_6H_4\cdot CH_2\cdot OH)_2$, are much less stable. In attempting to obtain the first of these from the methyl ester by the action of cold alcoholic soda, water is eliminated and *o*-indazylbenzoic acid,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{N\text{—}}{CH}}{>}N\cdot C_6H_4\cdot CO_2H,$$

formed; it melts at 204—205°. The second compound, *o*-azobenzyl alcohol decomposes spontaneously in the cold in acetone or alcohol solution, and *o-indazylbenzyl alcohol* is obtained melting at 56—57° and distilling at 250° under 20—25 mm. pressure. The presence of a $CH_2\cdot OH$ or CO_2H group in the ortho-position in the second benzene nucleus thus facilitates in a high degree the formation of indazyl derivatives.

H. M. D.

Formation of Diazo-compounds. ANGELO ANGELI (*Ber.*, 1904, 37, 2390—2391. Compare Abstr., 1901, i, 322; 1902, i, 765).—The action of benzenesulphohydroxamic acid and phenylhydroxylamine on α-naphthol in alcoholic potassium hydroxide solution leads to the formation of benzeneazo-α-naphthol.

G. Y.

The Limit of Coupling of Diazobenzene with Phenol. LÉO VIGNON (*Compt. rend.*, 1904, 138, 1278—1280).—The author obtains *p*-hydroxyazobenzene in 80 per cent. yield by coupling one molecule of phenol with one molecule of diazobenzene chloride. By employing two molecules of the latter, an 80 per cent. yield of phenolbisdiazobenzene, $OH\cdot C_6H_3(N_2Ph)_2$, is obtained, in which the diazo-groups occupy the ortho- and para-position relatively to the OH group. It crystallises in reddish-brown spangles, melts at 123—124°, and is readily soluble in ether or light petroleum, less so in alcohol, insoluble in water, but

readily soluble in alkali hydroxides. Attempts to couple a third molecule of diazobenzene chloride with phenol have given no result. The formation of the bisdiazo-compound thus appears to represent the limit of combination. H. M. D.

Azo-dye from Anthranilic Acid and *p*-Cresol. Badische Anilin- & Soda-Fabrik (D.R.-P. 151279).—Unlike other phenols, *p*-cresol, on combination with diazotised anthranilic acid, yields a reddish-yellow dye which gives a dark claret colour when mordanted with chromium salts. C. H. D.

[Azo-compounds from 2-Hydroxy-3-naphthoic Acid.] Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 151205).—Para-substituted derivatives of aminobenzene-*o*-sulphonic acid,

$$NH_2 \cdot C_6H_3X \cdot SO_3H,$$

in which $X = CH_3$, C_2H_5, NO_2, Cl, Br, or OMe, form soluble diazonium compounds which combine with 2-hydroxy-3-naphthoic acid to form red dyes. The sparingly soluble sodium salts of these dyes are readily converted into metallic lakes, which are very fast towards light. C. H. D.

[Benzorhodamines. Basic Dyes of the Triphenylmethane Series.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 150440).—Benzorhodamines are obtained by the condensation of benzaldehyde or its derivatives with monoalkyl derivatives of *o*-amino-*p*-cresol, conversion into pyrone derivatives, and oxidation. Thus, *o*-chlorobenzaldehyde condenses with *o*-methylamino-*p*-cresol sulphate to form the sulphate of a new *base*, crystallising in colourless needles. On heating with sulphuric acid or zinc chloride and adding alkali hydroxide, the *pyrone* is obtained as a red, crystalline mass. Ferric chloride oxidises it to the *benzorhodamine*, which forms red, felted needles, dissolving in water to a red solution with yellow fluorescence. Similar dyes are obtained from other substituted benzaldehydes. C. H. D.

Yellow Dyes of the Acridine Series. Badische Anilin- & Soda-Fabrik (D.R.-P. 151206).—Diaminoacridine derivatives, such as acridine-yellow and benzoflavin, are converted into new orange-yellow dyes by heating with twice their weight of glycerol for several hours at 150—180°. The hydrochlorides of the leuco-bases may also be employed. The new dyes, the nature of which is not yet determined, form reddish-brown powders dissolving readily in water. The solutions in concentrated sulphuric acid are brown, becoming green on warming. C. H. D.

Trisazo-dyes from 2 : 4-Diaminoacetanilide. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 151204).—2 : 4-*Diaminoacetanilide*, prepared by reduction of 2 : 4-dinitroacetanilide, melts at 158—159° and dissolves readily in water, sparingly in alcohol or benzene. Black trisazo-dyes are obtained by diazotising acetyl-*p*-phenylenediamine, combining with 7-amino-*a*-naphthol-3-sulphonic acid,

removing the acetyl group, preparing the tetrazo-compound, and combining with 2 mols. of the new base, or with 1 mol. of the new base and 1 mol. of a suitable diamine. C. H. D.

Fatty-aromatic Diazoamino-compounds (Triazens). LUDWIG WOLFF and HANS LINDENHAYN (*Ber.*, 1904, 37, 2374—2381).—*β-Cyano-α-phenyltriazen* (benzazocyanamide), $C_6H_5 \cdot N:N \cdot NH \cdot CN$, forms colourless flakes, which soon become yellow, melts at 72° with vigorous "puffing," and can be exploded by a blow or by contact with sulphuric acid. The *potassium* derivative, $C_7H_5N_4K,H_2O$, from which the cyanide was separated, was prepared by the action of potassium cyanide on diazobenzimide, $C_6H_5 \cdot N_3$; it forms colourless, silvery flakes, dissolves readily in water to an alkaline solution, and less readily in cold alcohol. The *silver*, *iron*, and *copper* derivatives are insoluble; the *barium* salt crystallises in broad, colourless needles. Reduction with zinc dust and ammonia gives phenylhydrazine; concentrated hydrochloric acid gives diazobenzene chloride and carbamide, whilst 10 per cent. potassium hydroxide gives ammonia, carbon dioxide, and aniline, but not phenol.

α-Cyano-β-phenyl-β-methyltriazen [methylanilinoazo cyanide],

$$NMePh \cdot N:N \cdot CN,$$

prepared by the action of methyl iodide on the potassium salt, crystallises from hot alcohol in nearly colourless flakes, melts at 69—70°, and dissolves in concentrated hydrochloric acid, but is reprecipitated by water. Aqueous sodium hydroxide decomposes it very rapidly at 60—70°, giving methylaniline, nitrogen, and sodium cyanate, whilst concentrated hydrochloric acid gives ammonia and methylaniline.

α-Phenyltriazen-β-thiocarbamide, $NPh:N \cdot NH \cdot CS \cdot NH_2$, prepared by the action of ammonia and hydrogen sulphide on the potassium derivative, crystallises from hot alcohol or chloroform in nearly colourless, glistening flakes or needles and decomposes at 110—111° with liberation of gas; it is very stable towards hot sodium hydroxide, but is decomposed by cold hydrochloric acid, giving diazobenzene and thiocarbamide. The *methyl* derivative, $NMePh \cdot N:N \cdot CS \cdot NH_2$, crystallises from hot alcohol in yellowish-red needles, detonates at 97°, and is decomposed by hydrochloric acid with gradual liberation of nitrogen.

T. M. L.

Chemical Nature of Histon and the Proteids from which it is Extracted. CARLO FOÀ (*Atti R. Accad. Lincei*, 1904, 13, i, 414—422).—The author gives, in a tabulated form, the principal reactions, some of which are new, of histon, acid albumin, proto-albumose, deutero-albumose, hetero-albumose, peptone, and ovo-protein. It is seen from this that histon has many reactions in common with acid-albumin, the proteoses, and peptones. When subjected to pepto-hydrochloric digestion for 48 hours, histon is transformed partly into proteoses and partly into peptones. Histon is formed by the action of dilute hydrochloric acid on the stroma of anucleated red corpuscles.

T. H. P.

Salmin and Clupein. ALBRECHT KOSSEL and HENRY D. DAKIN (*Zeit. physiol. Chem.*, 1904, **41**, 407—415. Compare this vol., i, 211, 355, and Abderhalden, *ibid.*, i, 463).—Further researches by the aid of Fischer's esterification method indicate the absence of alanine and leucine among the products of the hydrolysis of salmin.

The following numbers give the amounts of the various hydrolytic products obtained when the amount of salmin = 100. Arginine, 87·4; serine, 7·8; aminovaleric acid, 4·3; and pyrrolidine-2-carboxylic acid, 11·0.

The products obtained from clupein are arginine, aminovaleric acid, serine, alanine, and pyrrolidine-2-carboxylic acid. J. J. S.

Action of 4 per cent. Sulphuric Acid on Legumin. DMITRI PRIANISCHNIKOFF (*Landw. Versuchs-stat.*, 1904, **60**, 27—40).—Legumin is quickly decomposed by 4 per cent. sulphuric acid when heated, being converted into substances which are not precipitated by copper hydroxide. At the commencement, compounds are produced which are not precipitated by phosphotungstic acid, and after prolonged heating as much as two-thirds of the total nitrogen is in this form. It is probable that amino-acids are formed. Nitrogen as ammonia and as hexon bases also increase during the treatment, and represent finally a tenth and a fifth respectively of the total.

Peptones are produced at first in considerable quantity, but as the heating is continued are decomposed. N. H. J. M.

Action of Heat and Acidity on Amylase. PAUL PETIT (*Compt. rend.*, 1904, **138**, 1231—1233. Compare this vol., i, 541).—The liquefying and saccharifying activity of a slightly alkaline infusion of malt is increased by the addition of small quantities of lactic acid; at one stage of the addition a precipitate appears which increases at first with the acidity and then redissolves. The precipitate can be filtered, washed and dried; it acquires a brown colour, and when once dry does not dissolve readily in dilute acid or alkalis, whilst the filtrate gives the Schoenbein reaction, and liquefies and saccharifies starch paste. In a series of experiments, equal quantities of malt infusion neutralised with $N/50$ sodium carbonate were acidified with varying quantities of $N/50$ lactic acid, heated for 10 minutes in a water-bath, cooled and neutralised with $N/50$ sodium carbonate; the results showed that a quantity of acid had disappeared, the amount increasing with the initial acidity of the solution; thus if x denote the initial quantity of acid and y the variation in the acidity, $y = 0·4 - 0·337x$. The author assumes that the amylase displaced from an insoluble lactonic combination by means of the sodium carbonate forms a compound with the acid which is soluble in small quantities of acid, but is precipitated when the quantity of acid reaches a certain limit. M. A. W.

Hydrolysis of Ethyl Butyrate by Lipase. JOSEPH H. KASTLE, MARIUS EARLY JOHNSTON, and ELIAS ELVOVE (*Amer. Chem. J.*, 1904, **31**, 521—550).—It has been shown by Kastle and Loevenhart (Abstr., 1901, i, 178) that the activity of lipase solutions is greatly diminished by filtration, and this conclusion has now been confirmed by further

experiments. A solution of lipase was prepared by extracting fresh hog liver with water, and adding a small quantity of $N/100$ hydrochloric acid to the aqueous extract; the mixture was then heated to 40°, when a heavy, albuminous precipitate was produced. On filtering, a clear solution was obtained, the activity of which towards ethyl butyrate was not much more than one-half of that of the unfiltered extract. The residue left on filtration was found to be comparatively insoluble in water but readily soluble in 0·2 per cent. solution of sodium carbonate. This alkaline lipase solution is very active towards ethyl butyrate, but during hydrolysis gives rise to a heavy precipitate of coagulated proteid. This precipitate is not formed with clear solutions of the ferment prepared with very dilute acids (preferably butyric acid), and the latter were therefore used in the further study of the action of the enzyme on ethyl butyrate.

Clear solutions of lipase containing small quantities of hydrochloric or butyric acid are very stable, and can be kept for several weeks without showing any considerable decrease in lipolytic activity. They may be repeatedly filtered through paper without any loss of activity, but on filtration through a porous cup, the enzyme is completely removed and the solution rendered inactive.

A large number of experiments have been carried out with a view of determining the coefficient of velocity of the hydrolysis of ethyl butyrate by lipase under slightly varying conditions of concentration, temperature, and time. The velocity of the reaction during the first interval of 15 minutes is greatly diminished by the presence of free hydrochloric or butyric acid, but the coefficients of velocity during the succeeding intervals are practically the same in all cases, showing that the effect of these small quantities of acid on the enzyme is only temporary. Small amounts of free acids retard the action of the enzyme, but do not permanently impair its activity, whilst large quantities of acids completely destroy the ferment.

The nature of the hydrolytic change was investigated by van't Hoff's method, which depends on the effect of change of concentration on the velocity of the reaction. It was found that it is a unimolecular process which is influenced to a small extent by the acid produced in the hydrolysis. Alcohol slightly retards the action of the enzyme, but the quantities produced in the hydrolysis of dilute solutions are so small that their effect is negligible.

The velocity constants have been determined at 0°, 10°, 20°, 30°, and 40°, and found to increase considerably with rise of temperature. The average ratio of the velocities between one temperature and another 10° higher is as 1 : 1·69.

Lipase, whilst effecting the hydrolysis of ethyl butyrate, suffers no permanent alteration, but retains its activity unimpaired. The amount of ethyl butyrate hydrolysed by lipase is, within certain limits, independent of the concentration of the ester.

The comparative activity of lipase, hydrochloric acid, and sodium hydroxide towards ethyl butyrate was studied. The concentration of the lipase solution was determined by evaporating a portion of it to dryness at 110° and weighing the residue. It is not improbable that only a small proportion of this residue consists of the enzyme, but for

the purpose of comparison it was regarded as pure lipase. The results indicate that the power of lipase to hydrolyse ethyl butyrate in dilute solution is far greater than that of either sodium hydroxide or hydrochloric acid, but that the action of the enzyme on the ester more nearly resembles that of sodium hydroxide than that of hydrochloric acid. E. G.

Oxidising Ferments. Robert Chodat and Alexis Bach (*Arch. Sci. phys. nat.*, 1904, [iv], 17, 477—510. Compare Abstr., 1902, ii, 344; 1903, i, 219; and this vol. i, 359).—Two classes of substances are concerned in biological oxidations. Peroxides of the type HO·OH, in which the hydrogen is replaced, or partially replaced, by an inorganic or organic radicle, having the characters of a ferment. These the authors designate *oxygenases*. The other class consists of peroxydases, ferments which render peroxides active in a manner similar to the effect of hydrolytic ferments on water.

Catalase is not a true oxidising ferment, being neither a peroxide of the oxygenase type nor a ferment which renders active free or combined oxygen. Its only function is the decomposition of hydrogen peroxide.

Up to the present time, it has only been possible to oxidise the hydrogen of phenols, aldehydes, aromatic amines, and hydriodic acid. In the case of *o*-phenylenediamine, a simple condensation to diaminophenazine takes place (compare Ullmann, Abstr., 1903, i, 199). Many substances which occur in plants, such as arbutin, æsculin, and tannin, are readily oxidised by the same agents, and it is not impossible that the condensations of polysaccharides and alkaloids, &c., are due to similar oxidations. N. H. J. M.

Non-existence of Philothion, a Supposed Sulphur-reducing Enzyme. J. E. Abelous and H. Ribaut (*Bull. Soc. chim.*, 1904, [iii], 31, 698—701. Compare Pozzi-Escot, Abstr., 1902, i, 513, 580, 654, 655, 577; ii, 635; 1903, i, 670; this vol., i, 130; ii, 272. Rey Pailhade, Abstr., 1881, 1101; 1896, ii, 326; 1900, ii, 678. Abelous and Gerard, Abstr., 1900, ii, 226; Abelous and Aloy, this vol., ii, 188, and Loew, Abstr., 1901, i, 435).—The authors find that extracts prepared by maceration of the liver of the horse, or of beer yeast in water saturated with chloroform, possess even after ebullition for some minutes the property of producing hydrogen sulphide on the addition of sulphur. Further, the rate at which hydrogen sulphide is evolved from solutions containing albumin, yeast extract, and liver extract, on addition of sulphur, increases steadily with rise of temperature, and exhibits no optimum temperature below 125°, the maximum at which observations were made. They are of opinion, therefore, that Pozzi-Escot's assertion that the formation of hydrogen sulphide under these conditions is due to the activity of a reducing enzyme is unjustifiable. T. A. H.

Organic Chemistry.

Electrolytic Preparation of Bromoform. ERICH MÜLLER and RICHARD LOEBE (*Zeit. Elektrochem.*, 1904, 10, 409—414).—The authors have modified the method of preparation of bromoform described by Coughlin (Abstr., 1902, i, 197) by omitting the diaphragm. In order to avoid reduction of the acetone or of the products of the reaction, it is necessary to add potassium chromate to the solution. In order to get a good current efficiency, it is necessary to arrange the experiment so that a mixture of bromine and bromoform is produced; this is finally shaken with a solution of acetone and sodium carbonate until it is colourless; the current efficiency is then over 90 per cent. The conditions required are: a solution containing about 25 per cent. of potassium bromide, 12·5 per cent. by volume of acetone, and 0·2 per cent. of potassium chromate; current density at the platinum anode, 0·07 ampere per sq. cm. The bromoform is kept well mixed with the liquid and the alcohol-hydroxide formed is neutralised by a rapid current of carbon dioxide. T. E.

Addition of Hydrogen Haloids to Olefines in Acetic Acid and Aqueous Solutions. II. WLADIMIR N. IPATIEFF and W. N. DECHANOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 659—669).—In presence of acetic acid, ethylenic hydrocarbons combine readily with hydrogen bromide or iodide, but only slowly with hydrogen chloride. With hydrogen chloride and iodide, this combination always takes place according to the rule discovered by Markownikoff, but with hydrogen bromide a certain amount of abnormal product is always obtained. The proportion of abnormal product formed is different for different ethylenic hydrocarbons and becomes less as the difference between the amounts of hydrogen united with the carbon atoms on either side of the double linking increases. Thus, with *iso*butylene, containing the complex $\cdot C\!:\!CH_2$, the proportion of abnormal product is 6—7 per cent.; with trimethylethylene, containing $:C\!:\!CH\cdot$, 10—15 per cent.; and with *iso*propylethylene, containing $\cdot CH\!:\!CH_2$, 50 per cent. T. H. P.

Synthesis in the Amylene Series; αε-Diamyloxyamylene $(CH_2)_5(O\cdot C_5H_{11})_2$, αε-Dibromoamylene, and αε-Di-iodoamylene. JULES HAMONET (*Compt. rend.*, 1904, 138, 1609—1612. Compare this vol., i, 467).—αε-Diamyloxyamylene, $C_5H_{10}(O\cdot C_5H_{11})_2$, prepared by the action of amyloxybromomethane on the magnesium derivative of δ-bromo-α-amyloxybutane, is a mobile liquid boiling at 159—160° under 20 mm. or at 276—277° under 759 mm. pressure, has a sp. gr. 0·844 at 18°, and reacts energetically with hydrogen bromide to form *ε-bromo-α-amyloxyamylene*, $C_5H_{11}\cdot O\cdot[CH_2]_4\cdot CH_2Br$, a liquid boiling at 130—131° under 20 mm. pressure, not crystallising in a mixture of solid carbon dioxide and ether, and yielding a magnesium derivative,

$$C_5H_{11}\cdot O\cdot C_5H_{10}\cdot MgBr.$$

αε-*Dibromoamylene*, $C_5H_{10}Br_2$, prepared by the action of hydrogen bromide on αε-diamyloxyamylene at 100° in sealed tubes, is a liquid at the ordinary temperature, crystallises in a mixture of solid carbon dioxide and ether, the crystals melting at −34 to −35°; it boils at 111—112° under 20 mm. or at 221° under 763 mm. pressure, and has a sp. gr. 1·706 at 18°. The dibromoamylene prepared by Gustavson and Demjanoff (compare Abstr., 1889, 950) from pentamethylenediamine and boiling at 208—214° under the ordinary pressure is probably not the αε-compound. αε-*Di-iodoamylene*, $C_5H_{10}Br$, prepared in similar manner to the dibromo-compound, is a faintly colourless liquid boiling at 149° under 20 mm. pressure, having a sp. gr. 2·194 at 18°, and when cooled in a mixture of ice and salt, forming crystals which melt at 9°.

M. A. W.

Formation of Dimethyl*iso*propylcarbinol in the Hydrogenation of Acetone. GEORGES DENIGÈS (*Compt. rend.*, 1904, 138, 1607—1609).—In addition to *iso*propyl alcohol and pinacone, dimethyl*iso*propylcarbinol is also produced in the reduction of acetone by means of sodium according to the equation $2COMe_2 + 4H = CHMe_2{\cdot}CMe_2{\cdot}OH + H_2O$. In order to isolate the tertiary alcohol, which is formed only in small quantities, the reduction is effected at 0° in the presence of a saturated solution of potassium carbonate, the product washed with water, extracted with ether, and distilled. It passes over between 115° and 125° and is identical with the alcohol obtained by Grignard's synthesis from acetone and magnesium *iso*propyl bromide, or by Butleroff's method from zinc methyl and *iso*butyl chloride. It gives an orange precipitate, $\left(SO_4{<}{}^{Hg}_{Hg}{>}O\right)_3C_6H_{12}$, on boiling with an acid solution of mercuric sulphate, and a red explosive precipitate with mercuric nitrate (compare Abstr., 1900, i, 89) characteristic of tertiary alcohols.

Preliminary experiments seem to show that the production of a tertiary alcohol of twice the carbon content, in addition to a pinacone and a secondary alcohol of the same carbon content, is a general reaction in the hydrogenation of ketones of the paraffin series.

M. A. W.

A New Class of Ether Oxides. MARCEL DESCUDÉ (*Compt. rend.*, 1904, 138, 1703—1705).—*Diethoxymethyl oxide* [*diethoxymethyl ether*], $O(CH_2{\cdot}OEt)_2$, prepared, together with diethoxymethane, by the action of sodium ethoxide on dichloromethyl oxide (compare this vol., i, 546), is a colourless, mobile liquid with an ethereal odour, boils at 140°, has a sp. gr. 0·90781 at 25°/4°, n_D 1·38732, is soluble in the ordinary organic solvents, dissolves in ten times its weight of water, is decomposed by acids to form methanal and alcohol, and is not attacked by aqueous solutions of sodium or potassium carbonate. The molecular weight has been determined by the vapour density method, and also by the cryoscopic method in benzene or water. In view of these facts, the author concludes that the compound boiling at 102—106°, and having sp. gr. 0·864, obtained by Coops (compare Abstr., 1902, i, 77) by the action of alcohol on the product of the

reaction between hydrogen chloride and methanal is not diethoxymethyl oxide.

Dimethoxymethyl oxide, obtained similarly to the preceding compound, boils at 106—108°, has a sp. gr. 0·959 at 20°/20°, and forms a detonating mixture with oxygen at a red heat.

Corresponding derivatives of the higher alcohols could not be isolated owing to the decomposition which occurred on distilling the product of the reaction between dichloromethyl oxide and the sodium derivative of the alcohol. M. A. W.

Mixed Organo-inorganic Anhydrides. Luigi Francesconi and U. Cialdea (*Gazzetta*, 1904, 34, i, 435—446).—The authors describe the methods and apparatus used in the preparation and analysis of mixed nitroso-organic anhydrides obtained by the action of nitrosyl chloride on the silver salts of organic acids (Abstr., 1903, i, 788). The anhydrides are best purified by distillation in a stream of dry carbon dioxide; they are explosive, and hence difficult to analyse.

Nitrosyl propionate, COEt·O·NO, resembles nitrosyl acetate (*loc. cit.*) in physical and chemical properties. It has the normal vapour density, and decomposes rapidly in the light, yielding propionic and nitrous anhydrides and becoming green.

Nitrosyl benzoate, C_6H_5·CO·O·NO, is a yellow oil, very unstable towards light or heat; it readily absorbs moisture from the air, giving benzoic and nitrous acids. T. H. P.

Action of Hydrogen Peroxide on Anhydrides and the Formation of Organic Acid, Peroxides, and Peracids. Alphonso M. Clover and A. C. Houghton (*Amer. Chem. J.*, 1904, 32, 43—68. Compare Clover and Richmond, Abstr., 1903, i, 396).—When acetic peroxide is dissolved in an aqueous solution of hydrogen peroxide, peracetic acid is produced at the expense of the active oxygen of the hydrogen peroxide; the amount produced is greater than that which would be formed in the ordinary hydrolysis of an aqueous solution of acetic peroxide, and its formation takes place much more rapidly than in the latter case.

If acetic anhydride is dissolved in hydrogen peroxide solution, both peracetic acid and acetic peroxide are produced. A study of the rate of formation of these two substances shows that the peracetic acid is formed first, and that the peroxide is produced by the action of the peracetic acid on the anhydride. The action of hydrogen peroxide on acetic anhydride is much more rapid than that of water.

Propionic anhydride behaves towards hydrogen peroxide in the same way as acetic anhydride.

When an excess of succinic anhydride is added to a solution of hydrogen peroxide, a crystalline precipitate of *succinic peroxide acid*, $[CO_2H·CH_2·CH_2·CO·O]_2$, is produced, which is moderately soluble in water, alcohol, acetone, or ethyl acetate, and sparingly so in ether. This compound is colourless and odourless, crystallises in irregular flat plates, softens at 115°, melts and decomposes at 128°, and does not explode on percussion. Its production is due to the action of the persuccinic acid first formed on the succinic anhydride present. The

aqueous solution of succinic peroxide acid gradually undergoes hydrolysis with the formation of persuccinic and succinic acids. It causes the rapid liberation of iodine from potassium iodide, and oxidises a manganous salt to permanganic acid. When the peroxide acid is heated with boiling xylene, it undergoes decomposition with the formation of carbon dioxide, succinic anhydride, succinic acid, adipic acid, and a gummy acidic substance.

Persuccinic acid, $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CO_3H$, separates in large crystals from a mixture of chloroform and ether, melts and decomposes at 107°, and is soluble in water, alcohol, acetone, or ethyl acetate. When slowly heated, it undergoes decomposition with the formation of carbon dioxide and acrylic acid.

When a solution of persuccinic acid is treated with glutaric anhydride, a crystalline precipitate of *succinic glutaric peroxide acid*,

$$CO_2H{\cdot}[CH_2]_2{\cdot}CO{\cdot}O_2{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO_2H,$$

is produced, which softens at 105°, melts and decomposes at 107°, is readily soluble in alcohol, acetone, or ethyl acetate, and sparingly so in ether, and has a less powerful oxidising action than succinic peroxide acid.

Glutaric peroxide acid, $[CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O]_2$, obtained by the action of hydrogen peroxide on glutaric anhydride, is a crystalline substance which melts and decomposes at 108°, is freely soluble in alcohol, acetone, or ethyl acetate, and moderately so in benzene. When heated with boiling xylene, it undergoes decomposition with the formation of carbon dioxide and suberic acid. E. G.

Behaviour of Cyanogen towards Methylene Compounds. Wilhelm Traube (*Annalen*, 1904, 332, 104—158).—The addition of cyanogen to methylene compounds takes place in the presence of traces of sodium ethoxide; when the temperature is kept low, 1 mol. of cyanogen reacts with 1 mol. of the methylene compound, but when no cooling agent is employed, with 2 mols. Thus, ethyl acetoacetate yields ethyl cyanoiminomethylacetoacetate, or ethyl dicyanoacetoacetate, $CN{\cdot}C(:NH){\cdot}CHAc{\cdot}CO_2Et$, which exists in 2 or 3 isomeric forms, and combines with a second mol. of the ester to form a di-imino-compound (compare Abstr., 1898, i, 241, and 1899, i, 192). Acids react immediately with the substance first mentioned, alcohol being eliminated and a deep yellow substance produced, which is now represented by the formula $\begin{array}{l}CHAc{\cdot}CO\\ \,|\qquad\quad\,|\\ C(CN){:}N\end{array}$, and is therefore the anhydride (lactam) of the imino-acid (compare *loc. cit.*). This compound is also formed when the ethyl dicyanoacetoacetate is added to an alcoholic solution of ethyl sodioacetoacetate. Ethyl dicyanodimalonate, formed from cyanogen and 2 mols. of ethyl malonate, loses 2 mols. of alcohol under the influence of alkalis, the anhydride (lactam) thus produced being very stable. That these compounds are anhydrides and not *cyclo*pentene derivatives, as previously thought, is shown by the fact that under the influence of alkali hydroxides they yield acids containing nitrogen.

The di-imino-compounds, containing carbethoxy-groups, and other di-imino-compounds, as tetra acetyldi-iminobutane and dicyanodiacetyl-

acetone, yield cyclic compounds with elimination of water. These appear not to be pentene derivatives, as previously believed, but pyrrole derivatives with a tertiary nitrogen atom.

When two methylene compounds combine with 1 mol. of cyanogen, two different di-imino-compounds are formed, according to the order in which the methylene compounds are combined with the cyanogen; thus, ethyl dicyanoacetoacetate and ethyl malonate form a colourless additive product, but ethyl dicyanomalonate and ethyl acetoacetate form a yellow anhydride (lactam) with elimination of alcohol.

Action of Cyanogen on Ethyl Malonate [With C. HOEPNER.]—*Ethyl dicyanomalonate* (*ethyl cyanoimino*iso*succinate*), $C_9H_{12}O_4N_2$, is prepared by leading cyanogen into a well-cooled alcoholic solution of ethyl malonate containing a trace of sodium ethoxide, and forms crystals melting at 93°. If a solution of the ester in a concentrated alcoholic solution of ammonia is kept for 24 hours, *ethyl β-dicyanomalonate* separates in white needles melting at 123°. On treating the ester in alcoholic solution with hydrochloric or sulphuric acids, it is hydrolysed to the *acid ester*, $CN{\cdot}C(:NH){\cdot}CH(CO_2Et){\cdot}CO_2H$, which melts at 238°. When this compound is carefully heated at 100° with an aqueous solution of 2 mols. of sodium hydroxide and the liquid subsequently acidified with dilute sulphuric acid, the *dibasic acid ester*,

$$NH:C(CO_2H){\cdot}CH(CO_2Et){\cdot}CO_2H,$$

is obtained as colourless needles melting with evolution of carbon dioxide at 134°. The *sodium* salt forms leaflets. On reducing the dicyano-ester with 3 per cent. sodium amalgam in the presence of water, an asparagine *derivative*, $NH_2{\cdot}CO{\cdot}CH(NH_2){\cdot}CH(CO_2H)_2$, is formed, which crystallises out on addition of acetic acid; it melts and decomposes at 120°. The *dilactam* of ethyl dicyanodimalonate (*βγ-di-imino-adipyl-αδ-dicarbethoxydilactam*) is obtained by prolonged treatment of a solution of ethyl malonate in ethyl alcohol containing sodium ethoxide with cyanogen, and subsequent decomposition of the red sodium salt which separates with acids (compare Abstr., 1903, i, 76); the *disodium* salt crystallises in red crystals with $2H_2O$; the potassium salt forms purple-red crystals with $2H_2O$. When boiled with alkalis, hydrolysis takes place, *βγ-di-iminoadipyl-αδ-dicarboxylic acid*,

$$C_2[(:NH){\cdot}CH({\cdot}CO_2H)_2]_2,$$

being formed as yellow needles (compare *loc. cit.*). A *dimethyl* derivative of the foregoing dilactam is obtained by treatment of the sodium salt in the presence of alcohol with methyl iodide; it crystallises in deep yellow needles melting at 150°; the corresponding *ethyl* compound crystallises in yellow needles melting at 156°; both these compounds react violently with ammonia, yielding diamino-compounds.

The *lactam* of ethyl dicyanomalonoacetoacetate, $C_{13}H_{16}O_6N_2$, is prepared by adding to a solution of ethyl dicyanomalonate a solution in alcohol of ethyl acetoacetate containing sodium ethoxide; on acidification, the ester separates and crystallises; it forms yellow needles, beginning to melt at 103° and is completely molten at 137°. The corresponding *methyl* derivative, $C_{14}H_{16}O_6N_2$, is obtained by using ethyl sodiomethylacetoacetate, and crystallises in yellow needles melting at 139°. The corresponding *benzoyl* derivative, $C_{18}H_{18}O_6N_2$, is similarly prepared from ethyl sodiobenzoylacetoacetate and forms

yellow needles melting at 194°. The *lactam* of ethyl dicyanomalono-acetosuccinate, $C_{17}H_{22}O_8N_2$, is prepared from ethyl acetosuccinate and ethyl dicyanomalonate, and forms yellow crystals melting at 116°. Ethyl dicyanomalonate and acetylacetone condense in a similar manner in the presence of sodium ethoxide, forming the lactam, $C_{12}H_{14}O_5N_2$, which crystallises in dark yellow needles melting at 135°.

All attempts to hydrolyse these lactams by means of alkalis did not result in crystalline compounds, the action of aqueous hydrochloric acid led to the production of the di-imino-compounds, which, in their turn, were decomposed into a methylene compound and the cyanoimino-compound, ethyl dicyanomalonate.

Action of Cyanogen on Ethyl Acetoacetate and Acetylacetone [With M. Braumann.]—When ethyl α-dicyanoacetoacetate is dissolved in alcoholic ammonia, an *amidine*, $C_8H_{13}O_3N_3$, separates after long keeping, which forms yellowish-white crystals decomposing at 209—211°, and is an additive product of ammonia and ethyl dicyanoacetoacetate in mol. proportions. On warming ethyl α-dicyanoacetoacetate with acidified water to 60°, *ethyl α-acetyl-α′-iminosuccinamate*, $C_8H_{12}O_4N_2$, is produced by addition of water; it crystallises in leaflets melting at 142°. On treating the ester last mentioned with sodium hydroxide (1 mol.), *acetyliminosuccinimide*, $\begin{matrix} C(:NH)\cdot CO \\ | \\ CHAc—CO \end{matrix}\!\!>\!NH$, is produced on acidification in the form of plates which do not melt sharply. Its *methyl* derivative, $C_7H_8O_3N_2$, prepared by treating it in alcoholic solution with methyl iodide and sodium ethoxide, forms small, yellow crystals melting at 226—227°.

Ethyl β-dicyanoacetoacetate is obtained from the α-compound either by dissolving it in warm acetic acid and precipitating with water after cooling, or by dissolving in warm alcohol and passing in hydrogen chloride; this substance crystallises in rhombic plates melting at 178°, and combines with ammonia, not as does the isomeride, in mol. proportions, but in the proportion of 2 mols. of ester to 1 mol. of ammonia, 1 mol. of alcohol being eliminated, and the compound $C_{14}H_{17}O_5N_5$, which is crystalline and melts at 219°, being formed. *Ethyl γ-dicyanoacetoacetate* is prepared by treating the α-compound in alcoholic solution with ethylaniline or other secondary bases; it forms colourless crystals melting at 211°. Whilst the α-ester is decomposed with the formation of hydrocyanic acid and the β-ester remains unchanged when treated with methyl iodide and sodium ethoxide in alcoholic solution, the γ-ester yields *ethyl dicyanomethylacetoacetate*, $C_9H_{12}O_3N_2$, which crystallises in colourless needles melting at 110—113°.

Ethyl β-dicyanodiacetoacetate is obtained from the ordinary ethyl dicyanodiacetoacetate (ethyl αδ-diacetyl-βγ-di-iminoadipate) by the action of sodium amalgam; the oily reduced product is removed by ether, and the alkaline liquor acidified, when the β-compound separates in colourless needles melting at 132·5°; it gives no coloration either with sulphuric or hydrochloric acid or with ferric chloride, whilst the α-ester yields respectively a purple-red, a dirty-green and a wine-red coloration with these reagents. The α-ester is dissolved by alkali hydroxides with a yellowish-red coloration, alcohol being eliminated and the lactam produced, which is precipitated on acidifying. The

β-ester, on the other hand, forms a colourless solution in alkalis and is reprecipitated unchanged by acids. The reduced product previously mentioned is *ethyl βγ-diamino-αδ-diacetylvalerate*,

$$CH_2Ac\cdot CH(NH_2)\cdot CH(NH_2)\cdot CHAc\cdot CO_2Et;$$

it forms colourless needles melting at 35°, and has marked basic properties.

The *lactam*, prepared from ethyl dicyanodiacetoacetate by the regulated action of alkalis, forms dark yellow needles melting at 136°, and dissolves in alkali hydroxide unchanged, forming a reddish yellow solution which decomposes on keeping. When the lactam is heated with a solution of 8 per cent. sodium hydroxide (6 mols.), *dicyanodiacetoacetic acid* (*αδ-diacetyl-βγ-di-iminoadipic acid*),

$$CO_2H\cdot CHAc\cdot C(:NH)\cdot C(NH)\cdot CHAc\cdot CO_2H,$$

separates in colourless needles on acidification, and melts with evolution of carbon dioxide at 230°. A study of the nearly allied *ethyl α-carboxy-δ-acetyl-βγ-di-iminoadipate*,

$$CHAc(CO_2Et)\cdot C(:NH)\cdot C(:NH)\cdot CH(CO_2Et)_2,$$

shows that this compound is not converted into a lactam by alkalis, but is partly hydrolysed into an *ester acid*, $C_{13}H_{18}O_7N_2$, which contains one carboxy-group, is crystalline, and melts at 160°. Attempts to eliminate the nitrogen from this ester failed. Hydrochloric acid was without action; when the ester was simultaneously treated with nitrous and hydrochloric acids, half the nitrogen was eliminated, but instead of the expected compound $C_{15}H_{21}O_8N$, the *substance* $C_{15}H_{23}O_8N$, which crystallised in colourless needles melting at 110°, was formed.

β-Dicyanoacetylacetone (*cyanoiminomethylacetylacetone*) is obtained by the action of acetic acid or very dilute hydrochloric acid on the α-compound, and crystallises in pale yellow needles melting at 227°. The corresponding *γ-compound* is obtained when the α-compound is treated with the molecular quantity of ethylaniline in alcoholic solution, and separates as insoluble plates melting at 211°. The δ-*compound* is yellowish-green, melts at 162°, and is scarcely soluble in sodium hydroxide. The α-compound is characterised by the fact that it is easily decomposed by alkali hydroxides into hydrocyanic acid and cyanoacetylacetone, and is alone able to combine with methylene compounds and bases. By sulphuric acid, the α compound is destroyed, whilst the isomerides form coloured solutions; the α-compound alone gives a coloration with ferric chloride.

Dicyanodiacetylacetone (symmetrical *αδ-tetra-acetyl-βγ-di-iminobutane*) is most readily prepared by warming a mixture of acetylacetone, dicyanoacetylacetone, and sodium ethoxide in alcoholic solution. *Ethyl α-carboxy-βγ-di-imino-δδ-diacetylvalerate*,

$$CHAc_2\cdot C(:NH)\cdot C(:NH)\cdot CH(CO_2Et)_2,$$

is prepared from mol. quantities of ethyl sodiomalonate, and dicyanoacetylacetone, and forms white prisms melting at 141—142°.

Action of Cyanogen on Ethyl Benzoylacetate [With FELIX HEINEMANN.]—*Ethyl dicyanobenzoylacetate* (*ethyl cyanoiminomethylbenzoylacetate*), $CN\cdot C(:NH)\cdot CHBz\cdot CO_2Et$, is prepared by passing cyanogen into a cooled alcoholic solution of ethyl benzoylacetate and sodium ethoxide, and forms crystals melting at 142·5°; when kept in

contact with aqueous sodium hydroxide, hydrocyanic acid, and ethyl cyanobenzoylacetate, $CN\cdot CHBz\cdot CO_2Et$, are formed; the latter melts at 37·5°. The dicyano-ester is very stable towards acids, but treatment with hot concentrated sulphuric acid converts it into an isomeride which crystallises in insoluble needles melting at 184°. The ester yields an *additive* product with ammonia, $C_{13}H_{15}O_3N_3$, which forms prismatic crystals melting at 176°, and an *aniline* derivative, $C_{19}H_{19}O_3N_3$, which crystallises in hexagonal leaflets melting at 155°. The *additive* product with hydrogen sulphide, $C_{13}H_{14}O_3N_2S$, forms prismatic, yellow crystals melting at 160°, which rapidly become greenish-yellow; the compounds with bases are probably amidines.

Hydroxylamine (2 mols.) and ethyl dicyanobenzoylacetate (1 mol.) react with the elimination of 1 mol. of H_2O, 1 mol. of the hydroxylamine combining directly with the cyano-group and the other reacting with the carbonyl group of the ester; the compound thus formed, $C_{18}H_{16}O_4N_4$, forms colourless crystals melting and decomposing at 155°.

The *phenylhydrazone* of ethyl dicyanobenzoylacetate, $C_{19}H_{18}O_2N_4$, is crystalline and melts at 163°; the *acetyl* compound, $C_{15}H_{14}O_4N_2$, crystallises in colourless plates melting at 111°. *Ethyl dicyanodibenzoylacetate* (*ethyl βγ-di-imino-αδ-dibenzoyladipate*), $C_{24}H_{24}O_6N_2$, prepared by treating ethyl dicyanobenzoylacetate with sodium ethoxide and ethyl benzoylacetate, crystallises in leaflets melting at 156·5°.

Action of Cyanogen on Ethyl Cyanoacetate and Benzoylacetone [With W. SANDER.]—*Ethyl dicyanocyanoacetate* (*ethyl cyanoiminomethylcyanoacetate*), $CN\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et$, prepared by passing cyanogen into a cooled alcoholic solution of ethyl cyanoacetate and sodium ethoxide, crystallises in yellow needles melting and decomposing at 162°. When molecular quantities of this ester and ethyl sodioacetoacetate are brought together in alcoholic solution, the *lactam* of ethyl dicyanocyanoacetoacetoacetate, $CO_2Et\cdot CHAc\cdot C\begin{matrix}\diagup C(:NH)\cdot CH\cdot CN \\ \diagdown N\text{———}CO\end{matrix}$, is obtained as a yellow, crystalline substance, sintering at 149° and melting completely at 168°. A similar *lactam*, $C_{10}H_9O_3N_3$, is obtained from ethyl dicyanocyanoacetate and acetylacetone by dissolving the two constituents in an alcoholic solution of sodium ethoxide and adding a dilute solution of sulphuric acid; it crystallises in yellowish-green plates melting at 175°. *Dicyanobenzoylacetone* (*cyaniminomethylbenzoylacetone*), $CN\cdot C(:NH)\cdot CHAcBz$, is prepared by passing cyanogen into a well-cooled solution of benzoylacetone and sodium ethoxide in alcohol; it crystallises in yellow prisms melting at 118° or 121°; the hydrogen sulphide *additive* product, $C_{12}H_{12}O_2N_2S$, forms yellow needles melting and decomposing at 182°. K. J. P. O.

Condensation of Bromoacetyl Glycol [α-Bromoethyl Acetate] with the Esters of Acetoacetic and Acetonedicarboxylic Acids. ALBIN HALLER and F. MARCH (*Compt. rend.*, 1904, **139**, 99—101. Compare Abstr., 1901, i, 538; 1903, i, 318, 714; this vol., i, 180).—*Methyl γ-acetoxy-α-acetylbutyrate*,

$$OAc\cdot CH_2\cdot CH_2\cdot CHAc\cdot CO_2Me,$$

prepared by heating a molecular mixture of the sodium derivative of methyl acetoacetate and α-bromoethyl acetate at 140—150°, is a liquid boiling at 150—153° under 12 mm. pressure, and reacts with semicarbazide to form the *3-methyl-4-acetoxyethylpyrazone-1-carboxylamide*, $OAc\cdot CH_2\cdot CH_2\cdot CH<\begin{matrix}CO—N\cdot CO\cdot NH_2\\ CMe:N\end{matrix}$, which crystallises from alcohol and melts at 163°. *Ethyl γ-acetoxy-α-acetylbutyrate*, similarly prepared to the methyl ester, boils at 147—150° under 13 mm. pressure and yields with semicarbazide the same pyrazolone as the methyl derivative. *Methyl α-acetoxyethylacetonedicarboxylate* (*methyl β-keto-γ-acetoxy-α-acetoxyethylbutyrate*),

$$OAc\cdot CH_2\cdot CO\cdot CH(CH_2\cdot CH_2\cdot OAc)\cdot CO_2Me,$$

prepared by heating a mixture of α-bromoethyl acetate and the sodium derivative of methyl acetonedicarboxylate at 120° for 1 hour, is an oil boiling at 152—155° under 20 mm. pressure.

Ethyl α-acetoxyethylacetonedicarboxylate, similarly prepared from ethyl acetonedicarboxylate, is an oil boiling at 162—165° under 20 mm. pressure. *Methyl γε-dihydroxy-β:(δ or ζ)-dicarbomethoxyphenylacetate*, $CO_2Me\cdot CH_2\cdot C_6H(OH)_2(CO_2Me)_2$, melting at 143—143·5°, is a secondary product in the preparation of methyl α-acetoxyethyldicarboxylate; and, similarly, ethyl γε-dihydroxydicarbethoxyphenylacetate (compare Cornelius and Pechmann, Abstr., 1886, 802) is formed in the preparation of the ethyl derivative. M. A. W.

Normal Presence of Formaldehyde in the Products of Combustion and Smoke. AUGUSTE TRILLAT (*Compt. rend.*, 1904, 138, 1613—1615).—Various combustible substances, coal, peat, different kinds of wood, paper, pure cellulose, cork, caoutchouc, various tissues, and tobacco, were burnt in glass tubes in a current of air carefully purified from traces of formaldehyde, the gaseous products condensed in suitable receivers, and tested for formaldehyde by the dimethylaniline test; in all cases, formaldehyde was found in quantities varying from 1/1000 of the weight of the substance burnt to 1/100,000, the maximum quantity being given by the combustion of wood and cellulose materials. Similar results were obtained by the combustion of hydrocarbons; in the case of the aromatic series, the quantity of formaldehyde formed increased with the complexity of the homologue, thus benzene gave 1/120,000 of its weight of formaldehyde; toluene, 1/80,000; and xylene, 1/40,000 (compare Abstr., 1903, i, 222). Further, the nature of the walls of the furnace plays an important part in determining the amount of formaldehyde formed during combustion; from 12 grams of benzene burnt in a tube containing broken porcelain 0·0007 gram of formaldehyde was obtained, whilst from the same weight of benzene burnt at the same temperature in a tube filled with copper turnings, 0·078 gram was obtained. These experiments show that the formaldehyde present in atmospheric air (compare Henriet, this vol., i, 289, 649) is derived from the products of combustion.

M. A. W.

Combined Sulphurous Acids. WILHELM KERP (*Chem. Centr.*, 1904, ii, 57—58; from *Arb. Kais. Ges.-A.*, 21, 180—225).—Dextrose

sodium hydrogen sulphite, $C_6H_{12}O_6,NaHSO_3$, prepared by passing sulphur dioxide for a long time into a solution of dextrose and sodium carbonate in water and precipitating with alcohol, crystallises in matted needles and is readily soluble in water and rather soluble in methyl alcohol. The aqueous solution is acid to litmus, and is oxidised much more readily on exposure to air than the acetaldehyde compound; on evaporation, a syrup is left, which gradually crystallises.

The dissociation constants of the hydrolytic decomposition of the sodium hydrogen sulphite compounds of the following substances have been determined, and are given below:

	N-Solution.	1/10 *N*-Solution.	1/30 *N*-Solution.
Formaldehyde......	$0·13 \times 10^{-6}$	$0·12 \times 10^{-6}$	$0·11 \times 10^{-6}$
Acetaldehyde	$2·84 \times 10^{-6}$	$2·26 \times 10^{-6}$	$2·06 \times 10^{-6}$
Benzaldehyde	—	$1·00 \times 10^{-4}$	$1·10 \times 10^{-4}$
Acetono	$4·57 \times 10^{-3}$	$4·3 \times 10^{-3}$	$3·8 \times 10^{-3}$
Dextrose	311×10^{-3}	220×10^{-3}	124×10^{-3}

Under similar conditions, the quantities of free sodium hydrogen sulphite present in aqueous solutions of the compounds of acetaldehyde, benzaldehyde, acetone, and dextrose are respectively about 5, 31, 155, and 500—1200 times as great as that contained in a solution of the formaldehyde compound.

Rost has found that the combined sulphurous acid in these compounds has no characteristic pharmacological effect, the action being entirely due to the free sulphite. The poisonous action of these compounds can thus be approximately estimated by titrating the aqueous solution with iodine. Experiments have also shown that under certain conditions the physiological action of sulphurous acid contained in musts or fruits in which it is present as the dextrose compound is different to that of the acid present in wine in the form of the acetaldehyde compound.

The hydrolytic decomposition of the dextrose compound has also been determined by means of the polaristrobometer. The results show that whilst the normal and seminormal solutions give practically the same dissociation constant, a decinormal solution yields a very much lower value. E. W. W.

Rare Earths. Wilhelm Biltz (*Annalen*, 1904, 331, 334—358).—The thorium, didymium, praseodymium, neodymium, samarium, cerium, and lanthanum derivatives of acetylacetone can be prepared in nearly quantitative yields by adding solutions of salts of the earths to a faintly alkaline solution of acetylacetone in ammonia, and precipitating by addition of the smallest possible quantity of ammonia (compare Urbain, Abstr., 1897, i, 236; and Urbain and Budischorsky, 1897, ii, 318). These compounds could not be used as a means for separating or identifying the rare earths, since not only do they closely resemble one another in solubility, but they also very readily form additive products with ammonia or substituted ammonias. The melting points are as follows: *thorium acetylacetone*, 171°; *didymium acetylacetone*, 151—152° (from alcohol), 146—147° (from water),

142—144° (from carbon tetrachloride); *praseodymium acetylacetone*, 146°; *neodymium acetylacetone*, 144—146°; *samarium acetylacetone*, 146—147°; *cerium acetylacetone* (with $3H_2O$), 145° (anhydrous), 131—132°; *lanthanum acetylacetone*, 185° (from alcohol). In several cases, the melting points are neither constant nor sharp.

Cryoscopic determinations of the mol. weight in organic solvents show that these substances are generally dimolecular. Alcoholysis of the more feebly basic earths was observed; in the case of thorium, it could be quantitatively followed.

Aluminium acetylacetone, which has been long known, differs from the compounds here described by not being able to form additive compounds with ammonia and having a simple mol. weight in carbon disulphide.

Owing to the stability and ease of purification of thorium acetylacetone, an attempt was made to redetermine the atomic weight of thorium by its means, but it was found in practice that it is impossible to ignite thorium oxide over the blowpipe to a constant weight. Absorption of air or gas appears to take place.

K. J. P. O.

Metallic Derivatives of Acetylacetone. WILHELM BILTZ and JOHN A. CLINCH (*Zeit. anorg. Chem.*, 1904, 40, 218—224).—*Zirconium acetylacetone*, $ZrR_4,10H_2O$ (where R represents the acetylacetone residue, $C_5H_7O_2$), is best prepared by adding acetylacetone gradually to an aqueous solution of zirconium nitrate, sufficient sodium carbonate being simultaneously added to keep the acetylacetone in solution. The solution must be kept faintly acid. The salt separates in hexagonal crystals. The anhydrous salt separates from ethyl alcohol in needles, softens at 185°, and melts at 194—195°. *Uranium acetylacetone*, UR_4, prepared by reducing uranyl acetate by sodium hydrogen sulphite and then adding acetylacetone, separates from ether in brown or olive-green leaflets and melts indefinitely at 176°. *Uranyl acetylacetone*, UO_2R_2,H_2O, prepared by the action of acetylacetone on solutions of uranyl salts, is orange-yellow.

Determinations of the molecular weight of zirconium acetylacetone in carbon tetrachloride by the ebullioscopic method gave figures corresponding with ZrR_4. This behaviour is exceptional, since other rare earth derivatives of acetylacetone undergo polymerisation in organic solvents.

Thorium acetylacetone aniline, $(ThR_4)_2,NH_2Ph$, can be crystallised from ether without undergoing decomposition.

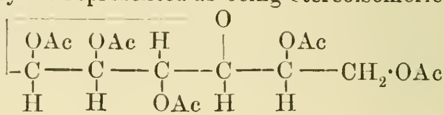
Didymium acetylacetone pyridine, DiR_3,C_5H_5N, melts at 144—145°. *Cobalt acetylacetone ammonia*, $CoR_2,(NH_3)_2$, forms a brown, crystalline precipitate. *Nickel acetylacetone ammonia*, $NiR_2,(NH_3)_2$, forms pale blue crystals. *Cobalt acetylacetone pyridine*, $CoR_2,(C_5H_5N)_2$, forms dark red crystals and melts at 150—152°. *Cobalt acetylacetone aniline*, $CoR_2,(NH_2Ph)_2$, forms brown, silky needles and melts at 108°. *Nickel acetylacetone pyridine*, $NiR_2,(C_6H_5N)_2$, forms blue crystals. *Nickel acetylacetone aniline*, $NiR_2,(NH_2Ph)_2$, forms pale blue needles.

A. McK.

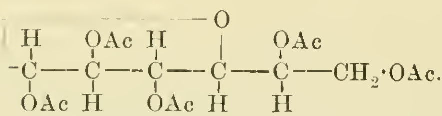
Birotation of Dextrose. Robert Behrend and Paul Roth (*Annalen*, 1904, **331**, 359—382).—In order to ascertain the cause of the birotation of dextrose, the subject has been investigated anew.

In pyridine solution, the birotation is very marked; $[\alpha]_D$ is at first 138·88°; after 3 hours at the temperature of the room, 127·87°; and after 24 hours, 71·17°. This fact excludes all possibility of the hydrate theory, since it is extremely improbable that pyridine can form an additive product with dextrose. It seems more probable that dextrose may exist in various isomeric forms of different optical activity.

A relation has been shown to exist between the various penta-acetates and the dextroses of different optical activity. Only two penta-acetates appear to exist, the α-compound melting at 110—111°, and the β-penta acetate melting at 130—131°. The γ-penta-acetate described by Tanret (Abstr., 1895, i, 321, 490), melting at 86°, appears to be a mixture of the α- and β-varieties. They are represented as being stereoisomeric in the sense of the formulæ:



and



When dextrose (m. p. 146°), which, when dissolved in water or pyridine, shows the higher rotation, is digested in pyridine with acetic anhydride, an acetyl derivative is obtained (m. p. 103—107°), from which the α-compound can be easily isolated. Keeping at the ordinary temperature increases the yield, whilst heating causes a decrease.

The β-penta-acetate is obtained, although in small yield, from a solution of dextrose in pyridine, which has acquired the lowest rotation either by heating or by keeping at 0° for 24 hours. Long keeping after the acetylation increases the yield. When solid dextrose is treated with pyridine and acetic anhydride, the same crude product is obtained.

It would appear, therefore, that since the crystalline dextrose (m. p. 146°) and the solution of higher rotation yield the α-penta-acetate, the α-compound has the same constitution as the dextrose of higher rotation. This is best expressed by giving dextrose the oxidic constitution. The solution of lower and constant rotation, which yields mainly the β-penta-acetate, contains a mixture in equilibrium of the two stereoisomerides.

It is suggested that the two dextroses should be called the α- and β-dextroses; the α-compound then corresponds to Tanret's α-dextrose, whilst the β-glucose is Tanret's γ-compound. The β-dextrose of Tanret is probably a mixture of the α- and β-dextroses. That the solution of lower and constant rotation contains a mixture of the α- and β-compounds is supported by the fact that the yield of β-penta-acetate obtained from it is but small.

It is further pointed out that it is possible that the α-dextrose is the aldehydic form of the sugar, and that the solution of constant rotation

contains either a mixture of the stereoisomeric oxidic forms, possibly in equilibrium with a certain amount of the aldehyde, or possibly a mixture of the aldehyde with β-dextrose.

Quantitative experiments on the acetylation have shown that theoretical yields are never obtained. From the solution of higher rotation, 79 per cent. of acetyl derivative is isolated, and from the solution of lower rotation, 66 per cent. From the former, about 64 per cent. of pure α-penta-acetate can be isolated by recrystallisation, and from the latter about 28 per cent. of β-penta-acetate can be obtained. Especial experiments were made to ascertain the properties of mixtures of α- and β-penta-acetates and it was thus found that the material obtained by acetylating dextrose consisted entirely of these two substances.

It has been found that the two dextrose acetates can probably be separated by the action of nitric acid when the β-compound is alone nitrated (compare Koenigs and Knorr, Abstr., 1902, i, 135). The nitration was effected by adding phosphoric oxide to a cooled solution of the sugar in nitric acid of sp. gr. 1·52. K. J. P. O.

Inulin. Arthur L. Dean (*Amer. Chem. J.*, 1904, **32**, 69—84).—Inulin has been prepared from *Dahlia variabilis*, *Inula helenium*, *Helianthus tuberosus*, *Lappa minor*, and certain species of *Solidago*; the products showed no essential differences and may therefore be regarded as identical; in each case, the inulin was found to be accompanied by lævulins. A determination of the molecular weight of inulin by the cryoscopic method gave a value 2329, but the experiment was inconclusive; the inulin employed had $[\alpha]_D$ $-38·6°$.

Inulin cannot be obtained with $[\alpha]_D$ much higher than $-40°$; such preparations appear to be unstable, and their rotatory power decreases on solution and reprecipitation. It is suggested that inulin is not a single, well-defined compound, but a mixture of molecular complexes which exhibit only slight differences in their properties. The lævulins are more soluble than inulin, have a smaller rotatory power, and are probably composed of complexes of smaller magnitude. E. G.

Molecular Weight of Glycogen. Madame Z. Gatin-Gruzewska (*Compt. rend.*, 1904, **138**, 1631—1634).—Using the Nernst-Abegg apparatus and a Beckmann thermometer capable of being read to the 1/1000th and estimated to the 1/10,000th of a degree, the author has redetermined the molecular weight of glycogen by the cryoscopic method. The glycogen was extracted from dog's liver, carefully purified, and dried over calcium chloride (compare this vol., i, 295). 3·850 grams of the substance in 200 c.c. of aqueous solution gave a freezing point of 0·0001°, which corresponds with a molecular weight of 716,100, or, applying the correction obtained from comparative experiments on sugar candy, the molecular weight of glycogen is over 140,000. The author therefore concludes (1) that the hitherto accepted value (1620) for the molecular weight of glycogen, due to Sabrieff (compare Abstr., 1890, 1215), is incorrect, and (2) either glycogen is very slightly

soluble in water and its molecular weight is infinitely great, or it is insoluble in water and its molecular weight has not been determined.

M. A. W.

Constitution of Ammonium. JOSEPH A. LE BEL (*J. Chim. Phys.*, 1904, ii, 340—346).—The author had previously obtained two crystalline forms of trimethyl*iso*butylammonium platinichloride, but the forms are reversible and dependent on temperature, and hence chemical isomerism is not definitely established. He has therefore endeavoured to obtain other substituted ammonium salts which exist in two forms, and finds that methyltripropylammonium platinichloride, however prepared, at first yields birefrangent crystals which, in 24 hours, change to regular octahedral crystals. The ethyltripropylammonium compound also forms two sets of crystals, but the stability of those first formed is less, the change occurring within a quarter of an hour. The author, however, considers both these to be cases of polymerisation and not of isomerism, and hence that the four radicles united to ammonium occupy the same position.

L. M. J.

Constitution of the So-called Dithiocyanic Acid and Perthiocyanic Acid. ARTHUR HANTZSCH and M. WOLVEKAMP (*Annalen*, 1904, 331, 265—297).—Since, under the action of concentrated hydrochloric acid, the esters of dithiocyanic acid yield mercaptans and ammonium chloride exclusively, no alkylamine being formed, the older formulæ, which represent the alkyl group as being linked to the nitrogen, cannot be correct. The formula $SM'\cdot C<\substack{N \\ N}>C\cdot SM'$ does not appear to be correct for the salts, since, in addition to the decomposition of the esters just mentioned, the esters and salts of dithiocyanic acid are only able to combine with 1 mol. of water or hydrogen sulphide. It is more probable that a true cyano-group is present, thus $C(SM')_2{:}N\cdot CN$, this supposition being in accord with the reaction of the esters just mentioned. Moreover, this formula accounts for the fact that the alkali salts are able to combine with hydrogen sulphide to form thiocarbamidodithiocarbonates, $C(SM')_2{:}N\cdot CS\cdot NH_2$; finally, the synthesis of dithiocyanates from cyanamide and carbon disulphide in an alkaline alcoholic solution clearly shows that dithiocyanates are cyanoaminodithiocarbonates, $CS_2 + CN\cdot NH_2 + 2KOH = C_2N_2S_2K_2 + 2H_2O$.

The free acid, which can be obtained from its salts in the form of yellow needles by treatment with hydrochloric acid at a low temperature, may have either the formula $C(SH)_2{:}N\cdot CN$ or $SH\cdot CS\cdot NH\cdot CN$; the latter is the more probable, since the acid, in spite of its low solubility, is not immediately precipitated by acids from its salts; further, the yellow colour points to a change of constitution.

The *dimethyl* ester, $C(SMe)_2{:}N\cdot CN$, prepared from methyl iodide and the potassium or silver salt, crystallises in colourless leaflets melting at 57°, and is converted by warming with concentrated hydrochloric acid into *methyl carbamidodithiocarbonate*, $C(SMe)_2{:}N\cdot CO\cdot NH_2$, which crystallises in white, stellate groups decomposing without melting at 217°. The formation of the same ester, in which both the alkyl groups

must be united to sulphur, from both the potassium and silver salts indicates that the salts are derivatives of an acid of the first type. The lead and silver salts decompose on heating into metallic sulphide and a yellow substance of low melting point, which is probably *cyanothiocarbimide*, $S{:}C{:}N{\cdot}CN$.

The cyanoamidocarbonates, prepared from cyanamide, carbon dioxide, and alcoholic potassium hydroxide, have probably the formula $(OM')_2C{:}N{\cdot}CN$, and not $(OM'){\cdot}CO{\cdot}NM{\cdot}CN$, as previously suggested.

The fact that the alkyl perthiocyanates decompose into ammonia and mercaptan, no alkylamine being formed, points to the alkyl group being linked to sulphur. This fact was demonstrated in the case of the *dimethyl* ester, which is easily obtained pure in the form of crystals melting at 42° and boiling at 279°. The esters of perthiocyanic acid are more stable than those of cyanoamidodithiocarbonic acid, and do not form additive compounds with water. Similarly, the perthiocyanates are more stable than the cyanoamidodithiocarbonates; they neither form additive compounds with hydrogen sulphide nor decompose with the formation of metallic sulphides. These facts indicate that the perthiocyanates are represented by a ring formula,

$$\begin{array}{l} C(SH){-}S \\ \| \\ N{\cdot}C(SH) \end{array}\!\!>N.$$

The solid acid obtained from the perthiocyanates, xanthanic acid, does not possess the same constitution as the salts, but is probably represented by the formula $\begin{array}{l} \overset{(ii)}{S}{-\!\!-}\overset{(i)}{S} \\ | \\ CS{\cdot}NH \end{array}\!\!>C{:}NH$. Only such rings containing two atoms of sulphur in which the two atoms of sulphur are directly linked are decomposed by alkalis with the separation of sulphur; xanthanic acid is decomposed by potassium hydroxide into potassium cyanoaminodithiocarbonate and sulphur, the sulphur atom (i) in the above formula being most probably set free. Xanthanic acid and aniline readily react, giving phenyldithiobiuret and sulphur; in this case, the sulphur atom (ii) is probably set free, thus:

$$\begin{array}{l} \overset{(ii)}{S}{-\!\!-}\overset{(i)}{S} \\ | \\ CS{\cdot}NH \end{array}\!\!>C{:}NH + NH_2Ph = NHPh{\cdot}CS{\cdot}NH{\cdot}C(SH){:}NH + S.$$

The other possible formula for xanthanic acid, $\begin{array}{l} S{-\!\!-}S \\ | \\ C(SH){:}N \end{array}\!\!>C{:}NH$, is not in accord with the indifferent character of the substance.

The transformation of xanthanic acid into salts of perthiocyanic acid through the intermediate stage of cyanoaminodithiocarbonate, which combines with the sulphur set free by the alkali, can be followed in certain cases.

The *acetyl* derivative of xanthanic acid, $\begin{array}{l} S{-\!\!-}S \\ | \\ CS{\cdot}NH \end{array}\!\!>C{:}NAc$, prepared by direct acetylation, undergoes, under the influence of alkalis, the same decomposition as xanthanic acid.

The constitution of xanthanic acid above demonstrated shows that it may be called 5-*thio*-2-*imino*-3 : 4-*disulphoazolidine*.

Thiuret (Fromm, Abstr., 1893, i, 575) is shown to be a sulphoazo-

lidine derivative, since it can be obtained by oxidising phenyldithiobiuret and is reconverted into that substance by reduction, and is decomposed by alkali hydroxides in the same way as xanthanic acid, sulphur and a salt of phenyliminocyanoaminothiocarbonate,

$$NPh{:}C(SM){\cdot}NH{\cdot}CN,$$

being formed. The esters obtained from the salts of the acid last mentioned are identical with those obtained from the product of condensation of phenylthiocarbimide and sodium cyanoamide. The alkyl group must be attached to the sulphur atom and the compound have either the formula $NPh{:}C(SAlk){\cdot}NH{\cdot}CN$ or

$$NHPh{\cdot}C(SAlk){:}N{\cdot}CN.$$

The salts of phenyliminocyanoaminothiocarbonic acid are not able to recombine with sulphur as are those of cyanoamidodithiocarbonic acid.

The so-called oxides and sulphides of the thiocarbimides (Freund, Abstr., 1895, i, 576) probably both have five-membered rings; thus the oxides have the formula $\begin{matrix} S{-}{-}S \\ | \\ CO{\cdot}NR \end{matrix}\!\!>C{:}NR$, and the sulphides the formula $\begin{matrix} S{-}{-}S \\ | \\ CS{\cdot}NR \end{matrix}\!\!>C{:}NR$. On reduction, they behave as does xanthanic acid, yielding dialkylthiocarbamides. The oxides react with aniline, phenylthiobiuret and sulphur being formed.

The sulphides, which are feebly basic, do not react with aniline, because it is not possible for them to assume the tautomeric form with the group $N{:}CSH$, as is the case with xanthanic acid, or it is possible that they pass on heating into a more stable form (as was observed by Freund in the case of the dimethyl ester) which no longer contains the disulphoazole ring, but is a diazosulphole derivative. These sulphides may, however, have the formula $\begin{matrix} S{-}NR \\ | \\ CS{\cdot}NR \end{matrix}\!\!>CS$.

The diazosulpholidine and the disulphoazolidine compounds may be distinguished by their different behaviour towards reducing agents, aniline, and alkalis. The latter yield with reducing agents thiocarbamides, with aniline, sulphur is eliminated, and with alkali, sulphur is set free and cyanoamido-derivatives are formed. The former, on the other hand, react with aniline, are not reduced to thiocarbamides, and do not lose sulphur under the influence of alkalis.

K. J. P. O.

Solubilities and Polymerisation of Cyanogen. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 1649—1652).—The author has examined the behaviour of cyanogen towards various solvents with the following results. (1) Water at 20° absorbs the gas slowly, but indefinitely; decomposition of the solution occurs at the same time with liberation of carbon dioxide. (2) Absolute alcohol at 20° absorbs cyanogen rapidly, but indefinitely, a brown precipitate is formed, and the liquid has a strong odour recalling that of carbylamine; by the action of water, two substances, one soluble and the other insoluble, are separated from the final product; the results of analyses of these two substances show that they are formed by polymerisation of the cyanogen and its condensation with alcohol. (3) Glacial acetic acid

absorbs 42 vols. of the gas per unit volume of liquid, the quantity rising to 50·5 vols. after 3 days; the solution contains free cyanogen, and, in addition, a small proportion of a polymerised product. (4) Chloroform absorbs 19 vols. of the gas per unit volume, the quantity rising to 29—30 vols. after some time; the solution contains free cyanogen. (5) and (6) Benzene and turpentine form solutions of cyanogen, containing respectively 28 and 9—10 vols. per unit volume.

M. A. W.

The Behaviour of Cyanogen towards Potassium Cyanide. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 138, 1653—1657).—Aqueous solutions of potassium cyanide absorb indefinite quantities of cyanogen, the potassium cyanide undergoes decomposition, the cyanogen is polymerised and carbon dioxide evolved; two substances were isolated from the final product, one insoluble, corresponding with the molecular *compound* $3CN,2H_2O$, and the other soluble, containing potassium. A solution of potassium ferrocyanide, or of potassium cyanide, in dilute acetic acid or alcohol also absorbs cyanogen with the formation of polymerised and condensation products.

M. A. W.

Thermochemical Studies on the Solution and Polymerisation of Cyanogen. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 139, 93—97. Compare preceding abstracts).—The heat developed by the solution of cyanogen in water is about 8·77 Cal. for each molecule of cyanogen, but owing to the polymerisation and chemical reaction which occur, the solution continues to develop heat slowly and at a decreasing rate, for some hours. The addition of a solution of potassium cyanide to an aqueous solution of cyanogen is accompanied by a heat development of 21·6 Cal. for each molecule of cyanogen. This is due to the polymerisation, condensation, and hydration induced by the action of the salt on the cyanogen. Alcohol dissolves cyanogen with a development of 9·28 Cals. for each molecule of cyanogen, and the addition of an alcoholic solution of potassium cyanide causes a further development of 5 Cals. for each molecule of cyanogen, or 81·2 Cals. for the ratio $KCN + 16CN_2$.

M. A. W.

Hydroxamic Acids. LUIGI FRANCESCONI and A. BASTIANINI (*Gazzetta*, 1904, 34, i, 428—434).—The amides of the monobasic acids with low molecular weight, such as acetamide, propionamide, and butyramide, react readily with hydroxylamine hydrochloride at the ordinary temperature yielding the corresponding hydroxamic acids. Capronamide reacts with hydroxylamine hydrochloride only at 100°, but, if moistened with alcohol, at the ordinary temperature. Chloroacetamide, on heating, yields the corresponding chloroacetohydroxamic acid. Among the aromatic amides, benzamide does not react with hydroxylamine hydrochloride, even at 100°. Carbamide, oxamide, succindiamide, and phthaldiamide only react above 100°, at which temperature the products formed decompose.

Chloroacetohydroxamic acid, $CH_2Cl\cdot C(OH)\colon N\cdot OH$, crystallises from benzene in nacreous laminæ which melt and decompose at 108° and

dissolve in alcohol, water, or ether; it has a faintly acid reaction, colours ferric chloride solution an intense red, gives a voluminous green precipitate with copper acetate, and reduces Fehling's solution.

Butyrohydroxamic acid melts at 127°, is extremely soluble in alcohol or water, and gives an intensely red coloration with ferric chloride.

T. H. P.

Azines of Ethyl β-Ketocarboxylates. LUDWIG WOLFF (*Ber.*, 1904, 37, 2827—2836. Compare Abstr., 1903, i, 203; Betti, Abstr., 1903, i, 78; this vol., i, 533).—*Ethyl azoacetoacetate*,

$$N_2(:CMe\cdot CH_2\cdot CO_2Et)_2,$$

is obtained as an oil on the addition of hydrazine sulphate and sodium carbonate to ethyl acetoacetate in aqueous solution. It crystallises from dilute alcohol in colourless needles, melts at 47—48°, is easily soluble in ether, chloroform, or benzene, and gives a colour reaction with ferric chloride only after some time. It reacts with hydrazine in alcoholic solution to form 3-methylpyrazolone; when acted on by hydrochloric acid, it yields ethyl acetoacetate, 3-methylpyrazolone, and 5-ethoxy-3-methylpyrazole; with nitrous acid, it yields ethyl azo-*iso*nitrosoacetoacetate.

Methyl azoacetoacetate is an oil at −20°, gives a red coloration with alcoholic ferric chloride after some minutes, and is decomposed by cold aqueous sodium hydroxide or when heated to 170—200°, with formation of crystalline products. When acted on by cold dilute hydrochloric acid, it yields methyl acetoacetate, 3 : 4-dimethylpyrazolone, and 5-ethoxy-3 : 4-dimethylpyrazole.

Contrary to Betti's statement, the substance formed by the action of hydrazine on ethyl *iso*nitrosoacetoacetate is ethyl azo*iso*nitrosoacetoacetate, $N_2[:CMe\cdot C(NOH)\cdot CO_2Et]_2$, and not ethyl bisdiazoacetoacetate (*loc. cit.*). It crystallises in yellow plates, melts at 194°, and is converted slowly by cold mineral acids, quickly by warm alcoholic hydrochloric acid, into 4-*iso*nitroso-3-methylpyrazolone, which melts at 232°.

5-*Ethoxy*-3 : 4-*dimethylpyrazole*, formed by heating methyl acetoacetate with hydrazine sulphate in aqueous solution, crystallises in matted, colourless needles, melts at 93°, and forms the *nitroso-compound*, $N\lt\begin{matrix}CMe\text{—}CMe\\ \quad\ \ \Vert\\ N(NO)\cdot C\cdot OEt\end{matrix}$, which is obtained as a yellow, crystalline mass and melts at 34°.

3 : 4-Dimethylpyrazolone crystallises in colourless prisms and melts at 268°.

5-Ethoxy-3-methylpyrazole is formed along with 3-methylpyrazole when ethyl acetoacetate is heated with hydrazine sulphate in aqueous solution. It crystallises in glistening, white needles, melts at 66—67°, and is hydrolysed by sulphuric acid at 146—150° to 3-methylpyrazolone. The solution of the hydrochloride gives an oily precipitation with gold chloride and a crystalline precipitate with mercuric chloride. The *nitroso*-compound, $N\lt\begin{matrix}CMe\text{—}CH\\ \quad\ \ \Vert\\ N(NO)\cdot C\cdot OEt\end{matrix}$, is a yellow oil which solidifies to yellow crystals and melts at 40°, and is converted by warm water

or alcohol into the isomeric *substance* $N\begin{smallmatrix}\diagup CMe-C\cdot NO \\ \diagdown NH-\overset{\|}{C}\cdot OEt\end{smallmatrix}$. This is obtained in an unstable, green, crystalline modification which melts and decomposes at about 100° and changes, spontaneously or when dissolved in cold sodium hydroxide solution and reprecipitated by cold hydrochloric acid, into a stable modification which crystallises in delicate needles, melts and decomposes at 126—127°, is soluble in aqueous sodium carbonate, and yields *iso*nitrosomethylpyrazolone (m. p. 232°) when treated with cold dilute hydrochloric acid. G. Y.

Semicarbazones of *iso*Nitrosoketones and of Acyldinitrohydrocarbons. Giacomo Ponzio (*Gazzetta*, 1904, 34, i, 410—414).—iso*Nitrosodiethyl-ketone-semicarbazone*, $NOH\colon CMe\cdot CEt\colon N_2H\cdot CO\cdot NH_2$, crystallises from alcohol in white prisms melting and decomposing at 219° and is slightly soluble in acetic acid or water.

iso*Nitrosomethyl-propyl-ketone-semicarbazone*,

$$NOH\colon CEt\cdot CMe\colon N_2H\cdot CO\cdot NH_2,$$

crystallises from alcohol in long, white needles melting and decomposing at 222° and dissolves to a slight extent in acetic acid or water.

iso*Nitrosoethyl*-iso*butyl-ketone-semicarbazone*,

$$NOH\colon CMe\cdot C(CH_2\cdot CHMe_2)\colon N_2H\cdot CO\cdot NH_2,$$

crystallises from alcohol in white prisms melting and decomposing at 203° and is slightly soluble in water or acetic acid.

Propionyldinitroethane-semicarbazone,

$$CMe(NO_2)_2\cdot CEt\colon N_2H\cdot CO\cdot NH_2,$$

crystallises from chloroform in white prisms melting and decomposing at 147—148° and is soluble in alcohol, ether, or benzene.

Acetyldinitropropane-semicarbazone, $CEt(NO_2)_2\cdot CMe\colon N_2H\cdot CO\cdot NH_2$, separates from chloroform in white plates melting and decomposing at 143—144° and dissolves in benzene, water, alcohol, or ether. It is remarkable that, whilst the action of nitrogen peroxide on *iso*nitrosomethyl-propyl-ketone results in the replacement of the NOH group by N_2O_3, yielding amylketopseudonitrole, the action of nitrogen peroxide on the semicarbazone of this ketone transforms the NOH group into N_2O_4.

iso*Valeryldinitroethane-semicarbazone*,

$$CMe(NO_2)_2\cdot C(CH_2\cdot CHMe_2)\colon N_2H\cdot CO\cdot NH_2,$$

crystallises from chloroform in white prisms melting and decomposing at 148—149° and is soluble in alcohol, ether, or benzene. T. H. P.

Some Mixed Derivatives of Hypophosphorous Acid. Charles Marie (*Compt. rend.*, 1904, 138, 1707—1709. Compare Abstr., 1901, i, 635; 1902, i, 71, 255; 1903, i, 328, 379, 678).—The author has prepared the following acids either by the action of an aldehyde on a monoketone derivative of hypophosphorous acid, $OH\cdot CRR^1\cdot PO_2H_2$, or by the action of a ketone or another aldehyde on a monoaldehydic derivative of hypophosphorous acid, $OH\cdot RCH\cdot PO_2H_2$; (1) the *acid* $OH\cdot CMe_2\cdot PO_2H\cdot CHPh\cdot OH$, obtained by the action of benzaldehyde on the acid, $OH\cdot CMe_2\cdot PO_2H_2$, melts at 182°, is soluble in water, alcohol, or acetone, and insoluble in chloroform or benzene; (2) the *acid*

$$OH\cdot CMe_2\cdot PO_2H\cdot CH(C_6H_{13})\cdot OH,$$

obtained by the action of heptaldehyde on the *acid* $OH\cdot CMe_2\cdot PO_2H_2$,

crystallises in brilliant spangles melting at 131°, is soluble in alcohol or acetone, and almost insoluble in cold water or ether; (3) the *acid* $OH\cdot CMeEt\cdot PO_2H\cdot CH(C_6H_{13})\cdot OH$, similarly prepared to the preceding, has similar properties and melts at 147°; (4) the *acid*

$$OH\cdot CMePh\cdot PO_2H\cdot CHMe\cdot OH,$$

obtained by the action of acetaldehyde on the acid

$$OH\cdot CMePh\cdot PO_2H_2,$$

melts at 192°, is very soluble in methyl or ethyl alcohol, very slightly so in acetone, and almost insoluble in benzene or chloroform; (5) the *acid*, $OH\cdot CEt_2\cdot PO_2H\cdot CHPh\cdot OH$, obtained by the action of acetaldehyde on the acid, $OH\cdot CEt_2\cdot PO_2H_2$, melts at 192°, is very slightly soluble in warm water or acetone, soluble in methyl or ethyl alcohol, and insoluble in ether, chloroform, or benzene; (6) the *acid*

$$OH\cdot CMePr\cdot PO_2H\cdot CHPh\cdot OH,$$

obtained by the action of methyl propyl ketone on the acid

$$OH\cdot CHPh\cdot PO_2H_2,$$

melts at 170°, is soluble in methyl or ethyl alcohol, and insoluble in ether, benzene, or chloroform; (7) the *acid* $OH\cdot CMe_2\cdot PO_2H\cdot CHMe\cdot OH$, obtained by the action of acetaldehyde on the acid $OH\cdot CMe_2\cdot PO_2H_2$, melts at 132° and has the same solubility as the preceding compound; (8) the *acid* $OH\cdot CH_2\cdot PO_2H\cdot CHPh\cdot OH$, obtained by the action of benzaldehyde on the *acid* $OH\cdot CH_2\cdot PO_2H_2$, melts at 154°, is soluble in water, methyl or ethyl alcohol, and insoluble in ether, benzene, or chloroform; (9) the *acid* $OH\cdot CHPh\cdot PO_2H\cdot CH(C_4H_9)\cdot OH$, obtained by the action of *iso*valeric aldehyde on the acid $OH\cdot CHPh\cdot PO_2H_2$, melts at 203—205°, is soluble in boiling water, ethyl or methyl alcohol, or acetone, and slightly soluble in cold water or ether. M. A. W.

Methylarsine. VICTOR AUGER (*Compt. rend.*, 1904, **138**, 1705—1707. Compare this vol., i, 22).—*Methylarsine*, $(CH_3As)_4$, obtained by the action of sodium hypophosphite and sulphuric acid on sodium monomethylarsonate,

$$2H_3PO_2 + AsMeO(OH)_2 = 2H_3PO_3 + AsMe + H_2O,$$

is a pale yellow oil, boiling at 190° under 15 mm. pressure, has a high specific gravity, and a strong garlic odour; it does not mix with water, is slightly soluble in alcohol, dissolves in hot acetic acid, and is very soluble in benzene; is not attacked by alkali hydroxides; is oxidised to methylarsenoxide by hot strong sulphuric acid, or by exposure to the air, or very rapidly in benzene solution; nitric acid oxidises it to methylarsonic acid, the halogens form corresponding derivatives, $AsMeX_2$, and the alkyl iodides react more or less readily according to the equation $2AsMe + 3MeI = AsMeI_2 + AsMe_4I$. Methylarsine is readily polymerised by hydrochloric acid to a brownish-black powder resembling arsenic, insoluble in the ordinary solvents, readily oxidised by nitric acid to methylarsonic acid; at 160° it behaves like the liquid polymeride towards methyl iodide, and is quantitatively converted into arsenic and trimethylarsine by dry distillation in an atmosphere of hydrogen, $3AsMe = AsMe_3 + As_2$. The brown compound obtained by Bougault (Abstr., 1903, ii, 339) by reducing methylarsonic acid by hypophosphorus acid in the presence of hydrochloric acid was probably this polymeride of methylarsine, and not arsenic, as described.

Ethylarsine is a yellow oil which does not polymerise so readily as methylarsine. M. A. W.

[Cacodylic Acid. Reply to von Zawidzki.] ARTHUR HANTZSCH (*Ber.*, 1904, **37**, 2705—2708. Compare this vol., i, 381; and von Zawidzki, Abstr., 1903, i, 801; this vol., i, 564).—Largely polemical. It is pointed out that the concentration of hydroxyl ions in solutions of the acid must be less than in the case of water, and not greater, as stated by Zawidzki. The reaction with hydrochloric acid is most readily explained by supposing that a chloride is formed, and, as this is only slightly ionised, it is relatively stable. J. J. S.

Freezing Point of Nitrobenzene. FR. C. C. HANSEN (*Zeit. physikal. Chem.*, 1904, **48**, 593—595).—The freezing point of pure nitrobenzene is generally given as 5·3°, but it appears that such samples contain a trace of moisture, for after desiccation over concentrated sulphuric acid, or vigorous boiling for a few minutes and removal of the vapour, the freezing point rises to 5·7°. Benzene is similarly, although to a less extent, sensitive to traces of moisture. J. C. P.

Symmetric Diphenyl Derivatives. FRITZ ULLMANN [with EMILIO GILLI, OSCAR LOEWENTHAL, and GUSTAV M. MEYER] (*Annalen*, 1904, **332**, 38—81).—Diphenyl and substituted diphenyls can be most readily prepared by heating iodobenzene or substituted iodobenzenes with copper at a temperature of 210—220°; in the case of substances boiling below 220°, the material is enclosed in a sealed tube, whilst with substances of higher boiling point open vessels may be used. The copper was the "naturkupfer C" of the firm of Bernh. Ullmann & Co., of Fürth; the use of other metals, such as magnesium, zinc, iron, or silver, is not to be recommended. This method of preparing diphenyls is far superior to Fittig's method, as the yield is nearly quantitative, and the material free from impurity.

I. *Hydrocarbons.*—When equal weights of iodobenzene and copper are heated for three hours in a sealed tube at 230°, the product extracted with ether, and the residue from the ether recrystallised from alcohol, pure diphenyl in a yield of 82 per cent. is obtained. By Fittig's method, only 5 per cent. is obtained. 2 : 2′-Dimethyldiphenyl is prepared from *o*-iodotoluene (b. p. 207° under 726 mm. pressure; Kekulé records 211°, and Edinger and Goldberg 202°) and copper in the same manner, and purified by fractionation; it forms large crystals melting at 17·8° and boiling at 258° under 737·6 mm. pressure; Fittig gives the boiling point as 272°, Zincke and Luginin as 277—282°, and Jacobson as 245—260°. The yield amounted to 63 per cent. 3 : 3′-Dimethyldiphenyl is prepared by heating *m*-iodotoluene (b. p. 211° under 734 mm. pressure; according to Beilstein and Kuhlberg, it boils at 204°) with copper at 240°; it is a colourless oil boiling at 283° under 718 mm. pressure. 4 : 4′-Dimethyldiphenyl is obtained in a yield of 54 per cent. by adding copper slowly to molten *p*-iodotoluene (b. p. 213·5° under 733 mm. pressure)

at 210°, and then raising the temperature to 260°; the crystalline product is extracted with alcohol, when the diphenyl is obtained as leaflets melting at 122°, and boiling at 295° under 760 mm. pressure (compare Zincke and Weiler).

The dixylyls, prepared by Fittig (*Annalen*, 1868, **147**, 38), Oliveri (*Gazzetta*, 1882, **12**, 158), and O. Jacobson (*Ber.*, 1881, **14**, 2112), were not pure. 2 : 2′ : 4 : 4′-*Tetramethyldiphenyl* was prepared by adding copper to 4-iodo-1 : 3-dimethylbenzene (b. p. 230° under 742 mm. pressure) heated to 228—230°, and then raising the temperature to 260°; the hydrocarbon forms orthorhombic crystals [$a : b : c$ = 0·64075 : 1 : 0·50192] melting at 41° and boiling at 288° under 722 mm. pressure. 2-*Iodo*-1 : 4-*dimethylbenzene*, $C_6H_3IMe_2$, prepared by adding potassium iodide to diazotised *p*-xylidine, is a colourless liquid boiling at 230° under 722 mm. pressure (Edinger and Goldberg give the boiling point as 217°), and has a sp. gr. 1·5988 at 17°. 2 : 2′ : 5 : 5′-*Tetramethylbenzene*, prepared from the iodo-derivative just described, forms colourless crystals melting at 50° and boiling at 284° under 732 mm. pressure.

2 : 2′ : 4 : 4′ : 5 : 5′-*Hexamethyldiphenyl* is prepared from 5-iodo-1 : 2 : 4-trimethylbenzene, which is obtained from ψ-cumidine and forms crystals melting at 52° and boiling at 320° under 738 mm. pressure. 2 : 2′ : 4 : 4′ : 6 : 6′-*Hexamethyldiphenyl* could not be obtained by Jannasch and Weiler (Abstr., 1895, i, 604, and 1900, i, 213) by Fittig's method, but it was prepared although in somewhat small yield, by heating iodomesitylene with copper at 260—270°; it forms colourless, transparent, monoclinic crystals [$a : b : c$ = 1·2892 : 1 : ? ; β = 95°48′] melting at 100·5° and boiling at 296° under 735 mm. pressure.

2 : 2′-Dinaphthyl (m. p. 287°) was prepared from 2-iodonaphthalene in a yield of 67·5 per cent. by heating with copper. 4 : 4′-Diphenyldiphenyl was prepared from 4-iododiphenyl (prepared from 4-nitrodiphenyl, and forming crystals melting at 111°) by heating at 250—270° with copper and then extracting the product with benzene, when a yield of 82·5 per cent. was obtained (Noyes and Ellis, Abstr., 1896, i, 51, obtained a yield of 5 per cent. when sodium and *p*-bromodiphenyl were used); it forms lustrous leaflets melting at 320°, and does not give the coloration with sulphuric acid which the natural hydrocarbon, "benzerythrene," is observed to show—a coloration which must therefore be due to an impurity.

II. *Halogen Derivatives.*—When chloroiodobenzenes are heated with copper, only the iodine is eliminated, good yields of chlorodiphenyls being obtained. 3 : 3′-*Dichlorodiphenyl*, thus prepared, forms colourless, transparent crystals melting at 23° and boiling at 322—324°; the yield was 67 per cent. 4 : 4′-*Dichlorodiphenyl* was obtained in a yield of 82 per cent. from *p*-chloroiodobenzene, and melted at 148° and boiled at 315° (compare *Jahresbericht*, 1866, 463). 2 : 2′ : 4 : 4′-*Tetrachlorodiphenyl* was prepared from 1 : 3-dichloro-4-iodobenzene (obtained in the ordinary way from 2 : 4-dichloroaniline) and formed crystals melting at 83° and boiling at 350—360°. 2 : 2′ : 4 : 4′ : 6 : 6′-*Hexachlorodiphenyl*, prepared from 1 : 3 : 5-trichloro-2-iodobenzene (m. p. 55° and b. p. 297° under 735 mm. pressure), forms quadratic crystals melting at 112·5°.

Bromoiodobenzenes are only converted into diphenyls by heating with copper in a very imperfect manner ; 3 : 3′-dibromophenyl (m. p. 53°) was obtained in very small yield from *m*-bromoiodobenzene.

III. *Sulphonic Acid Derivatives.*—Neither the calcium salt, the amide, nor the anilide of *p*-iodobenzenesulphonic acid reacts with copper to form diphenyls, but *p*-iodobenzenesulphonmethylanilide, a compound in which no hydrogen remains attached to the nitrogen, does so react. p-*Iodobenzenesulphonic anilide*, $C_6H_4I{\cdot}SO_2{\cdot}NHPh$, prepared from the sulphonic chloride, crystallises in leaflets melting at 143° and is readily methylated by the use of dimethyl sulphate ; p-*iodobenzenesulphonmethylanilide*, $C_6H_4I{\cdot}SO_2{\cdot}NMePh$, crystallises in leaflets melting at 111°, and, when heated with copper at 210—240°, is converted into 4 : 4′-*diphenyldisulphondimethylanilide*, which forms grey leaflets melting at 187°.

IV. *Nitro-derivatives.*—The conversion of halogen nitrobenzenes into nitrodiphenyls has been previously described (Abstr., 1901, i, 586).

V. *Amino-derivatives.*—Only when the hydrogen atoms of the amino-group are replaced by an alkyl and a sulphonic group was it found possible to obtain amino-derivatives of diphenyl. *m*- and *p*-Iodoaniline, *p*-iodoacetanilide, and *p*-iododimethylaniline give negative results when heated with copper. p-*Toluenesulphon*-m-*iodoanilide*, $C_7H_7{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4I$, was prepared from *m*-iodoaniline and *p*-toluenesulphonic chloride, and forms colourless crystals melting at 128° ; by means of dimethyl sulphate, it was converted into p-*toluenesulphon*-m-*iodomethylanilide*, $C_7H_7{\cdot}SO_2{\cdot}NMe{\cdot}C_6H_4I$, which crystallises in colourless needles melting at 81°. *Di*-p-*toluenesulphon*-3 : 3′-*methylaminodiphenyl*, prepared from the preceding compound, forms white, lustrous crystals.

VI. *Phenol Derivatives.*—Although the iodophenols do not react readily with copper, the alkyl derivatives of the phenols give excellent yields of diphenyls. 2 : 2′-Dimethoxydiphenyl is obtained in a yield of 88 per cent. from *o*-iodoanisole (compare Jannasch and Kölitz, Abstr., 1898, i, 190 ; Diels and Bibergeil, Abstr., 1902, i, 219) ; it melts at 154° and gives, when heated with alcohol and fuming hydrochloric acid, diphenylene oxide. The p-*toluenesulphonic ester* of o-*iodophenol*, $C_6H_4I{\cdot}O{\cdot}SO_2{\cdot}C_7H_7$, was prepared from the *p*-toluenesulphonic ester of *o*-nitrophenol, which was reduced to the amino-compound, the latter diazotised, and then treated with potassium iodide ; it forms yellow plates melting at 73°. When heated with copper at 260° and the product extracted with alcohol, the p-*toluenesulphonic ester* of 2 : 2′-*dihydroxydiphenyl* was obtained ; it crystallises in colourless needles melting at 171°.

The benzoates of 3 : 3′-dihydroxydiphenyl have also been prepared by a similar method, but only small yields were obtained. The *m*-iodophenol was, after other attempts, prepared by Noelting and Stricker's method (Abstr., 1888, 262) from *m*-iodoaniline ; the benzoate, prepared by the Schotten-Baumann process, forms slightly coloured crystals melting at 70° ; when heated with copper at 215—260°, a small amount of the *benzoate* of 3 : 3′-*dihydroxydiphenyl* was obtained by extracting the product of the reaction with benzene ; it forms white needles melting at 92°.

4 : 4′-Dimethoxydiphenyl was obtained in a yield of 85 per cent. from *p*-iodoanisole and copper, and melted at 173° (compare Gillmeister, Abstr., 1898, i, 138). 4 : 4′-Diethoxydiphenyl was obtained in a similar manner from *p*-iodophenetole, and melted at 176° (compare Hirsch, Abstr., 1889, 510). In order to prepare 2 : 2′ : 5 : 5′-*tetramethoxydiphenyl*, 2-*iodo*-1 : 4-*dimethoxybenzene* was obtained by the usual methods from nitro-1 : 4-dimethoxybenzene as a yellow liquid boiling at 285° under 728 mm. pressure; the diphenyl, prepared in the usual manner with a yield of 93 per cent., formed pale yellow crystals melting at 104°, and, when boiled with 50 per cent. hydrobromic acid and stannous chloride, was converted into a tetrahydroxydiphenyl (diquinol; m. p. 237°), previously obtained by Barth and Schreder (Abstr., 1885, 520).

VII. *Carboxylic Acid Derivatives.*—*Methyl* 2 : 2′-*diphenyldicarboxylate* is very readily obtained in a yield of 82 per cent. by heating methyl *o*-iodobenzoate with copper at 200—260°, extracting the product with ether, and fractionating the residue; the substance melted at 74·5° (compare Schultz, *Annalen*, 1880, **203**, 98). *Methyl* m-*iodobenzoate*, prepared from *m*-iodobenzoic acid, crystallised in colourless needles melting at 50° and boiling at 276—277° under 739 mm. pressure, and was converted into methyl 3 : 3′-diphenyldicarboxylate by heating with copper at 260° and extracting the product with methyl alcohol; it melts at 104° (compare Bülow and von Reden, Abstr., 1899, i, 150). When boiled with 70 per cent. sulphuric acid, the ester is hydrolysed to 3 : 3′-diphenyldicarboxylic acid, which crystallises from nitrobenzene and melts at 356—357° (compare Griess, Abstr., 1888, 826, and Bülow and von Reden, *loc. cit.*). Methyl 4 : 4′-diphenyldicarboxylate was prepared from methyl *p*-iodobenzoate and formed colourless leaflets melting at 214° (compare Weiler, Abstr., 1899, i, 490).

VIII. *Aldehyde Derivatives.*—4 : 4′-*Dibenzylideneaniline*,

$$C_{12}H_8(CH:NPh)_2,$$

was obtained by converting anhydroaminobenzaldehyde into *p*-iodobenzaldehyde (compare Hantzsch, Abstr., 1894, i, 331), which was then combined with aniline, forming p-*iodobenzylideneaniline*, a substance crystallising in colourless leaflets melting at 93°; when heated with copper at 260° and the product extracted with boiling benzene, the diphenyl derivative was obtained in colourless leaflets melting at 215°. 4 : 4′-*Diphenyldialdehyde* was prepared from dibenzylideneaniline by treatment with hot alcoholic hydrochloric acid, and crystallises in leaflets melting at 145°; the *diphenylhydrazone*, $C_{26}H_{22}N_4$, crystallises in yellow needles melting at 274°, and the *dioxime*, $C_{14}H_{12}O_2N_2$, forms pale brown crystals melting at 204°.

IX. *Ketone Derivatives.*—The preparation of 4 : 4′-*dibenzoyldiphenyl*, which crystallises in colourless leaflets melting at 218°, was effected as follows: by treatment of bromobenzene with magnesium in ethereal solution, a solution of magnesium phenyl bromide was obtained and then boiled with *p*-iodobenzaldehyde; the product was decomposed by adding it to ice-cold sulphuric acid, the volatile material removed by distilling in steam, and p-*iodobenzhydrol*,

$$C_6H_4I\cdot CHPh(OH),$$

extracted from the residue by petroleum; it forms colourless needles melting at 71°, and when oxidised with acetic acid and sodium dichromate is converted into *p*-iodobenzophenone (m. p. 102°) (compare Hofmann, Abstr., 1891, 1236). By heating the iodo-ketone with copper at 250° and extracting the product with benzene, the diphenyl derivative is isolated.

X. *Quinoline Derivatives.*—6-Iodoquinoline reacts violently with copper when they are heated together at 220°, the temperature rising to 340°; from the product, 6 : 6′-diquinolyl can be extracted with alcohol; it crystallises in leaflets melting at 181°, whilst the diquinolyl, prepared from benzidine, melts at 178°.

XI. *Azo-derivatives.*—4 : 4′-Diphenylazodiphenyl is prepared by extracting with benzene the red product obtained by heating *p*-iodoazobenzene with copper at 250°; it crystallises in orange-red, lustrous leaflets melting at 233·5°, and is probably identical with the substance (m. p. 226°) prepared by Bamberger (*Ber.*, 1896, 29, 103).

K. J. P. O.

2-Benzoylfluorene and Retene. MAX FORTNER (*Monatsh.*, 1904, 25, 443—452. Compare Abstr., 1903, i, 177).—2-*Cyanofluorene*, formed by the action of cuprous cyanide on 2-diazofluorene chloride (Diels, Abstr., 1901, i, 522), crystallises in yellow needles, melts at 88°, and is hydrolysed by concentrated hydrochloric acid with formation of *fluorene-2-carboxylic acid.* This crystallises in needles and sublimes with partial decomposition above 260°. The *silver* salt is a white, flocculent precipitate; the *methyl* ester crystallises in white needles and melts at 120°. Successive treatment of fluorene-2-carboxylic acid with thionyl chloride and with aluminium chloride and benzene leads to the formation of the benzoylfluorene, which was previously obtained by the action of benzoic chloride on fluorene in presence of aluminium chloride, and must be 2-benzoylfluorene, $\begin{array}{l} C_6H_4\cdot C\cdot CH\cdot CH \\ | \quad\quad\; | \quad\quad\;\; | \\ CH_2-C\cdot CH\cdot CBz \end{array}$. On reduction, 2-benzoylfluorene yields 2-benzylfluorene, which is obtained by action of benzyl chloride on fluorene (Goldschmiedt, *Monatsh.*, 1881, 2, 443) or by reduction of fluorenoylbenzoic acid (this vol., i, 168).

Oxidation of fluorene-2-carboxylic acid with sodium dichromate and glacial acetic acid leads to the formation of Bamberger and Hooker's diphenyleneketonecarboxylic acid (Abstr., 1885, 906, 1070). The *methyl* ester crystallises in glistening, yellow needles and melts at 181°. Retene must therefore be 2-methyl-8-propyl- or 8-methyl-2-propyl-phenanthrene.

G. Y.

Aniline-toluidine Oil from Caucasian Naphtha. W. N. OGLOBLIN (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 680—711).—The author has investigated two samples of aniline-toluidine oil prepared by Nikiforoff's patents from Russian naphtha; one sample contained aniline with a little *o*-toluidine and the other aniline with *o*-, *m*-, and *p*-toluidines.

T. H. P.

ω-Cyanodimethylaniline. HANS BUCHERER (*Ber.*, 1904, 37, 2825. Compare Warunis and Sachs, this vol., i, 669).—ω-Cyanodimethyl-

aniline is prepared from sodium hydroxymethylenesulphonate, monomethylaniline, and potassium cyanide. A. McK.

Action of Dichloroacetic Acid on Aniline and the Toluidines. GUSTAV HELLER (*Annalen*, 1904, 332, 247—304).—The earlier work on the action of dichloroacetic acid on anilines, more especially on *o*-toluidine (Meyer, *Ber.*, 1883, 16, 925, 926, 2261) and on *p*-toluidine (Duisberg, Abstr., 1885, 543), is discussed and an account given of the attempts, both analytical and synthetical, to ascertain the constitution of the products.

Action of Di- and Tri-halogen Substituted Anilides on Aromatic Bases.—[With RICHARD EMRICH.]—When dichloroaceto-*p*-toluidide (1 part) is heated on the water-bath with *p*-toluidine, the air having free access, p-*methylisatin*-p-*tolylimide*, $\underset{C_6H_4Me\cdot N:C-C_6H_4Me}{\overset{CO\cdot NH}{|\quad\ \ |}}$, is produced (compare Duisberg, *loc. cit.*). When aniline is caused to interact with dichloroacetanilide in the same way, *dianilinoacetanilide*,

$$CH(NHPh)_2\cdot CO\cdot NHPh,$$

is obtained as needles sintering at 137° and melting at 141—142°. Dichloroacetanilide and *o*-toluidine react in a similar manner, the product *di-o-toluidinoacetanilide*, $C_{22}H_{23}ON_3$, crystallising in needles melting at 166 5—167·5°. Dichloroacetanilide and *p*-toluidine yield a mixture of substances, one of which is slightly soluble and crystallises in needles melting at 262·5°; dichloroacetoluidide and aniline, on the other hand, give dianilidoacet-*p*-toluidide. Trichloroacet-*p*-toluidide (which melts at 113°, compare Judson, *Ber.*, 1870, 3, 784) and *p*-toluidine give a mixture of substances, which in any case contain no isatin, and from which, by means of alcohol, an insoluble crystalline substance, *oxal*-p-*toluidide* (m. p. 263°), $C_2O_2(NH\cdot C_6H_4Me)_2$ (compare Hübner, *Annalen*, 1881, 209, 372) can be isolated. In a similar manner, trichloroacetanilide and aniline yield oxalanilide (m. p. 245°), no byproducts being formed in this case. Trichloroacetanilide and *p*-toluidine yield *phenyl*-p-*tolyloxamide*, $NHPh\cdot CO\cdot CO\cdot NH\cdot C_6H_4Me$, which crystallises in four-sided plates melting at 206°, and is also produced, but with greater difficulty, from trichloroaceto-*p*-toluidide and aniline.

Action of Dichloroacetic Acid on Aniline.—[With RICHARD EMRICH.]—Mol. proportions of dichloroacetic acid as potassium salt and aniline were heated at 100° in aqueous solution in the presence of sodium acetate for five to six hours, when an oil separates. This material yields two isomerides, dibasic acids, $[:C(CO_2H)\cdot C_6H_4\cdot NHAc]_2$; on extraction with hot 10 per cent. sodium acetate solution, the one separates from the cold sodium acetate solution, and the other only after acidifying; the former, the α-compound, crystallises from sodium acetate solution in pale yellow aggregates of microscopic crystals, whilst the β-compound, which also forms microscopic crystals, is distinguished from the α-compound by its different behaviour towards solutions of sodium acetate, in which it is more soluble, and towards dilute acids; the salts of both acids are similar and not characteristic; both acids become coloured at 270°, sinter, and then decompose. The α-acid is converted into the β-compound by dissolving in potassium hydroxide, the change beginning after one of the carboxyl groups is

neutralised. When either the α- or the β-compound is kept, partial transformation occurs. Both the α- and β-compounds give, in hydrochloric acid solution with formaldehyde, condensation *products*,

$$C_2(CO_2H)_2(C_6H_4{\cdot}N{:}CH_2)_2,$$

which in both cases form insoluble crystalline aggregates, decomposing at a high temperature. *Compounds* with salicylaldehyde, $C_{30}H_{22}O_6N_2$, have also been prepared as amorphous insoluble powders, decomposing on heating. The *acetyl* derivative, prepared from the β-acid, is crystalline. Both the α- and the β-acids can be diazotised, but the α-compound only with difficulty.

The *aniline* salt of anilinoglyoxylic acid, $NPh{:}CH{\cdot}CO_2H,NH_2Ph$, is formed either when a concentrated aqueous solution of glyoxylic acid is treated with aniline acetate, or when potassium dichloroacetate is heated in aqueous solution with potassium acetate and aniline acetate (compare Doebner, Abstr., 1900, i, 473); it crystallises in slender, white needles melting at 92—93°, and is immediately decomposed by acids and alkalis; all attempts to prepare an acid from this salt resulted in the α-acid just described.

Synthesis of Stilbene Derivatives.—[With KARL AMBERGER.]—4 : 4′-*Dinitrodicyanostilbene*, $C_2(CN)_2(C_6H_4{\cdot}NO_2)_2$, is prepared by adding to a solution of *p*-nitrobenzyl cyanide in methyl alcohol a solution of iodine in absolute ether and a solution of sodium methoxide in methyl alcohol; it crystallises in microscopic prisms melting at 268—269°, and dissolves in a solution of sodium methoxide with an intense violet coloration. On reduction with a solution of stannous chloride, it is converted into the corresponding *diamino*-compound, which crystallises in small plates or needles melting over 300°, when it also sublimes. 4 : 4′-*Dinitrostilbenedicarboxylic anhydride* is prepared from the dicyanide by hydrolysis in acetic acid solution by means of hydrochloric acid under pressure at 185—190°; it crystallises in needles or quadratic plates melting at 197°. 4 : 4′-*Diaminostilbenedicarboxylic acid*, prepared by reducing the dinitro-compound with ammonium sulphide, forms intensely red flocks.

2 : 2′-*Dinitrodicyanostilbene*, prepared in the same manner as the para-compound from *o*-nitrobenzyl cyanide, crystallises in needles, becoming coloured at 210° and decomposing at 265°; on reduction, the 2 : 2′-*diaminodicyanostilbene* is obtained as an insoluble solid, melting and decomposing at 265°; it could not be hydrolysed. 2 : 2′-*Dinitrostilbene-dicarboxylic acid* can only be prepared by hydrolysis of the dinitro-compound in acetic acid solution with hydrochloric acid, when the acid amide is produced; this substance is converted into the acid by boiling with dilute sodium hydroxide; the acid sinters at 232° and melts and decomposes at 237·5°.

The connection between molecular vibrations and those due to chemical reactions is discussed at length. K. J. P. O.

Elimination of Alkyl Groups from Secondary Amines. JULIUS VON BRAUN (*Ber.*, 1904, 37, 2812—2819).—The secondary amine, NHR_2, is converted first of all into the dialkylated amide, $R_1{\cdot}CO{\cdot}NR_2$. In the event of R_1 in this latter type containing a benzene, substituted benzene, or a naphthalene residue, the amide is

converted into the amide chloride, $R_1\cdot CCl_2\cdot NR_2$, which, when heated, undergoes decomposition in two stages, namely: (1) $R_1\cdot CCl_2\cdot NR_2 = R_1\cdot CCl:NR + RCl$ and (2) $R_1\cdot CCl_2\cdot NR_2 = R_1CN + 2RCl$, the latter reaction taking place at the more elevated temperature. When one of the alkyl groups attached to the nitrogen atom is aromatic, however, the reaction is confined to the first stage, one molecule of aliphatic alkyl chloride being eliminated, whilst the imide chloride, $R\cdot CCl:NR$ (where R is an aromatic group), remains, as such compounds are not decomposed by heat at relatively high temperatures. Since, accordingly, imide chlorides are converted by water into monalkylated amides, $R_1CO\cdot NHR$, which, on further hydrolysis, yield primary bases NH_2R, and since nitriles can be hydrolysed to ammonia, the reactions described by the author provide a method for converting a secondary amine, NHR_2, into a primary amine, NH_2R, and into ammonia.

Dimethylbenzamide, $COPh\cdot NMe_2$, reacts vigorously with phosphorus pentachloride at about 110°; methyl chloride is evolved, whilst the residue contains methylbenzimidechloride, $CPhCl:NMe$, boiling at 80—105° under 10 mm. pressure (the boiling point is not sharp, since a little benzonitrile is always present). By the action of water on the imide chloride, methylbenzamide, $COPh\cdot NHMe$, boiling at 167° under 11 mm. pressure, is formed.

When the action of phosphorus pentachloride on dimethylbenzamide is completed at 160—170°, the action proceeds further, a second molecule of methyl chloride being eliminated and benzonitrile being formed along with its polymerisation product, cyaphenin.

Diethylbenzamide, $COPh\cdot NEt_2$, is converted in an analogous manner into ethylbenzamide, $COPh\cdot NHEt$, which melts at 67°. Benzonitrile and cyaphenin are obtained where the action is conducted at a higher temperature.

Phenylmethylbenzamide, $COPh\cdot NMePh$, is converted similarly into the corresponding imide chloride, then into the amide, which, on hydrolysis, yields aniline.

Phenylbenzylbenzamide, $COPh\cdot NPh\cdot C_7H_7$, when similarly treated, yielded benzanilide and benzyl chloride.

Dimethyl-p-bromobenzamide, $C_6H_4Br\cdot CO\cdot NMe_2$, prepared by the action of *p*-bromobenzoyl chloride on dimethylamine, separates from ether in glistening crystals and melts at 72°; when heated with phosphorus pentachloride at 170°, it forms *p*-bromobenzonitrile.

Dimethyl-α-naphthylamide, $C_{10}H_7\cdot CO\cdot NMe_2$, when similarly treated, yields α-naphthonitrile. A. McK.

Isomerism of Asymmetric Tolylammonium Salts. EDGAR WEDEKIND and F. OBERHEIDE (*Ber.*, 1904, 37, 2712—2727. Compare Abstr., 1902, i, 277, 643; 1903, i, 517; this vol., i, 37).—*Methyl-ethyl-p-toluidine* is a pale yellow oil distilling at 218—220°; the *picrate* crystallises in yellow needles and melts at 78°. The base combines readily with allyl iodide yielding *p-tolylmethylethylallyl-ammonium iodide*, which crystallises from chloroform in colourless needles containing a molecule of chloroform and melting and decomposing at 140—142°.

Ethylallyl-p-*toluidine*, $C_6H_4Me \cdot NEt \cdot C_3H_5$, distils at 238° and its *picrate* crystallises in lemon-yellow needles melting at 111°. The base combines with methyl iodide, forming a vitreous mass which slowly crystallises. When the crude product is crystallised from chloroform, the compound melting and decomposing at 140—142° is obtained, which crystallises in rhombic prisms [$a:b:c = 0.8209:1:0.7549$].

p-*Tolylmethylethylallylammonium bromide* crystallises from a mixture of benzene and chloroform in colourless, monoclinic needles decomposing at 173—174°.

The *nitrate* crystallises from chloroform in large, colourless needles containing a molecule of chloroform and melting at 95—97°. The d-*camphorsulphonate* forms hygroscopic needles melting at 160—161°, and could not be resolved by fractional crystallisation from a mixture of acetone and ethyl acetate.

Methylallyl-p-*toluidine* is a colourless oil distilling at 230—232°; the *picrate* crystallises from alcohol in yellowish-brown needles melting at 124°. The base readily combines with benzyl iodide, yielding *benzyl*-p-*tolylmethylallylammonium iodide*, which is deposited from a mixture of alcohol and ether in colourless crystals melting at 144—146°.

Allyl-p-*toluidine*, obtained by the action of allyl iodide on sodium formotoluide and subsequent hydrolysis with concentrated hydrochloric acid, and purified by conversion into its nitroso-derivative, is an oil distilling at 232—234°. The *hydrochloride* melts at 131—132° and the *acid oxalate* at 150—151°. On treatment with benzyl iodide, the base is converted into *benzylallyl*-p-*toluidine*, which distils at 214—215° under 31 mm. pressure. The *picrate* crystallises from alcohol in lemon-yellow needles melting at 138°. The tertiary base combines with methyl iodide yielding the quaternary ammonium iodide which decomposes at 144—146°. This same compound is also formed by the union of allyl iodide and benzylmethyl-p-toluidine (Rabaut, Abstr., 1892, 313). Benzyl-*p*-tolylmethylallylammonium iodide crystallises from alcoholic solutions in triclinic prisms [$a:b:c = 0.7686:1:0.8663$; $\alpha = 88°37'$; $\beta = 105°18\frac{1}{2}'$; $\gamma = 84°5'$]; it separates from aqueous solutions in triclinic crystals of somewhat different form. The corresponding *bromide* forms colourless needles melting and decomposing at 146—147°; the *nitrate* decomposes at 134—136°, and the d-*camphorsulphonate* melts at 167—168°. No resolution by fractional crystallisation has been effected.

Benzyl iodide combines with ethylallyl-*p*-toluidine, yielding a crystalline *benzyl*-p-*tolylethylallylammonium iodide*, which crystallises from absolute alcohol in colourless needles decomposing at 114—116°.

Benzylethyl-p-*toluidine* distils at 226° under 26 mm. pressure as a viscid, yellow oil and yields a *picrate* melting at 138°. It combines slowly with allyl iodide, yielding an amorphous, quaternary salt.

J. J. S.

Benzenesulphoncyanoamides of Primary Bases. JULIUS VON BRAUN (*Ber.*, 1904, 37, 2809—2812).—Although benzenesulphoncyanoanilide is produced in a good yield by interaction of benzenesulphonanilide and cyanogen bromide in the presence of alkali, thus: $Ph \cdot SO_2 \cdot NPhNa + BrCN = NaBr + Ph \cdot SO_2 \cdot NPh \cdot CN$, the yield is not

always good in reactions of a similar type. The method cannot accordingly be employed as a general one for the purification of primary bases by converting the latter into cyanobenzenesulphonamides and then hydrolysing these.

Benzenesulphoncyanoanilide, $Ph\cdot SO_2\cdot NPh\cdot CN$, prepared from the sodium salt of benzenesulphonanilide and cyanogen bromide, melts at 66—67°.

*Benzenesulphoncyano-*p*-toluidide*, $Ph\cdot SO_2\cdot N(C_6H_4Me)\cdot CN$, melts at 88°.

*Benzenesulphoncyano-*p*-anisidide*, $Ph\cdot SO_2\cdot N(C_6H_4\cdot OMe)\cdot CN$, melts at 95—96°.

Benzenesulphoncyanomethylamide, $Ph\cdot SO_2\cdot NMe\cdot CN$, boils at 205° under 30 mm. pressure and melts at 45—46°.

Benzenesulphoncyanoethylamide boils at 195° under 15 mm. pressure.

o-*Chlorobenzenesulphonanilide* separates from alcohol in spear-shaped crystals and melts at 127°.

The cyanogen group in the amides described is very readily removed during hydrolysis. A. McK.

Action of a Trace of Certain Salts or of Alkali Hydroxides on Phenyl Carbonate. Robert Fosse (*Compt. rend.*, 1904, **139**, 141—143).—The trace of sodium carbonate which at 200—300° determines the conversion of phenyl carbonate into carbon dioxide, phenol, and phenyl *o*-phenoxybenzoate (compare Abstr., 1903, i, 485) can be replaced by sodium phosphate, arsenate, di- or tetra-borate, sodium or potassium hydroxide, sodium salicylate or ethoxide. The action of large quantities of sodium ethoxide or hydroxide on phenyl carbonate has been examined by Hentschel (compare Abstr., 1883, 589), who obtained sodium salicylate and phenetole in the first case, and sodium salicylate and phenol in the second. M. A. W.

Molecular Rearrangement of Aminophenyl Alkyl Carbonates. Henry T. Upson (*Amer. Chem. J.*, 1904, **32**, 13—43. Compare Stieglitz and Upson, this vol., i, 575).—p-*Nitrophenyl methyl carbonate*, $NO_2\cdot C_6H_4\cdot O\cdot CO_2Me$, obtained by the action of methyl chlorocarbonate on *p*-nitrophenol in alkaline solution, is a white, solid substance which melts at 111—112° and is soluble in ether or alcohol. When treated with stannous chloride and hydrochloric acid, it is converted into the *hydrochloride* of p-*aminophenyl methyl carbonate*, which, when left in water for several hours, shows no tendency to undergo molecular rearrangement. o-*Nitrophenyl methyl carbonate* is a yellow, mobile oil. The *hydrochloride* of o-*aminophenyl methyl carbonate* forms a white solid.

3-*Nitro-*p*-tolyl ethyl carbonate*, $NO_2\cdot C_6H_3Me\cdot O\cdot CO_2Et$, crystallises from alcohol and melts at 56°. By reducing this compound with tin and hydrochloric acid and subsequently boiling the solution, a mixture of 4-hydroxy-*m*-tolylurethane and carbonyl-*o*-amino-*p*-cresol is produced. If, however, the reduction is effected in the cold, and, after the addition of alkali, the product is extracted with ether and the ethereal solution is treated with dry hydrogen chloride, the *hydrochloride* of 3-*amino-*p*-tolyl ethyl carbonate* is obtained as a white precipitate which melts

and decomposes at 135—137°; the *platinichloride* melts and decomposes above 171°. When the hydrochloride is dissolved in water, it is gradually converted into 4-*hydroxy*-m-*tolylurethane*,

$$OH\cdot C_6H_3Me\cdot NH\cdot CO_2Et,$$

which melts at 101°. *Carbonyl*-3-*amino*-p-*cresol*, $C_6H_3Me{<}{}^{-O-}_{NH}{>}CO$, crystallises in white needles, melts at 128°, and is soluble in alcohol, ether, or chloroform.

4-*Nitro*-m-*tolyl ethyl carbonate*, obtained from 4-nitro-*m*-cresol, is a yellow oil which solidifies at −5°. The *hydrochloride* and *platinichloride* of 4-*amino*-m-*tolyl ethyl carbonate* were prepared; the aqueous solution of the hydrochloride deposits crystals of 3-*hydroxy*-p-*tolylurethane*, $OH\cdot C_6H_3Me\cdot NH\cdot CO_2Et$, which melts at 95° and is soluble in alcohol, ether, or chloroform.

6-*Nitro*-o-*tolyl ethyl carbonate* crystallises in yellow needles and melts at 32—33°. The *hydrochloride* of 6-*amino*-o-*tolyl ethyl carbonate* is very soluble in water; the *platinichloride* was prepared and analysed. 2-*Hydroxy*-m-*tolylurethane*, which gradually separates from an aqueous solution of the hydrochloride, crystallises in white needles, melts at 74—76°, and is soluble in alcohol or ether.

4-*Chloro*-2-*nitrophenyl ethyl carbonate* forms nearly white crystals and melts at 60°. The *hydrochloride* of 4-*chloro*-2-*aminophenyl ethyl carbonate*, $CO_2Et\cdot O\cdot C_6H_3Cl\cdot NH_2,HCl$, is obtained as a white solid and is insoluble in water; the *platinichloride* crystallises in yellow needles. When the hydrochloride is boiled with water, it is converted into 3-*chloro*-6-*hydroxyphenylurethane*, $OH\cdot C_6H_3Cl\cdot NH\cdot CO_2Et$, which forms white needles and melts at 136—137°; this compound is also obtained by the action of ethyl chloroformate on 4-chloro-2-aminophenol. If the urethane is heated for some time at 230°, it is decomposed with formation of *carbonyl*-4-*chloro*-2-*aminophenol*, which crystallises in white needles and melts at 184—185°.

6-*Chloro*-2 *nitrophenyl ethyl carbonate* was obtained as an oil which did not solidify when cooled to −15°. The *hydrochloride* of 6-*chloro*-2-*aminophenyl ethyl carbonate* melts and decomposes at 126—127°, and is soluble in alcohol, but insoluble in water. When heated with water, it is converted into 5-*chloro*-6-*hydroxyphenylurethane*, which crystallises in needles and melts at 92—93°.

4-*Bromo*-2-*nitrophenyl ethyl carbonate* crystallises from ether in large, transparent plates and melts at 76°. The *hydrochloride* of 4-*bromo*-2-*aminophenyl ethyl carbonate* melts at 136—137°. 3-*Bromo*-6-*hydroxyphenylurethane* crystallises in white needles and melts at 140—142°.

4 : 6-*Dichloro*-2-*nitrophenyl ethyl carbonate* is a yellow solid which melts at 38—39°. The *hydrochloride* of 4 : 6-*dichloro*-2-*aminophenyl ethyl carbonate* melts and decomposes at 132—135° and is soluble in alcohol but insoluble in water; it is readily converted into 3 : 5-*dichloro*-6-*hydroxyphenylurethane*, which melts at 125° and may also be obtained by the action of ethyl chloroformate on 4 : 6-dichloro-2-aminophenol.

4-*Chloro*-6-*bromo*-2-*nitrophenyl ethyl carbonate* crystallises in yellow prisms and melts at 48—49·5°. The *hydrochloride* of 4-*chloro*-6-*bromo*-2-*aminophenyl ethyl carbonate* melts and decomposes at 131—132° and

is insoluble in water. 3-*Chloro*-5-*bromo*-6-*hydroxyphenylurethane* melts at 116—118°.

5-*Bromo*-3-*nitro*-o-*tolyl ethyl carbonate* melts at 61—62° and is soluble in alcohol, ether, or chloroform. The *hydrochloride* of 5-*bromo*-3-*amino*-o-*tolyl ethyl carbonate* is soluble in alcohol and insoluble in water, darkens at 137—143°, and melts and decomposes at 173—178°. 5-*Bromo*-2-*hydroxy*-m-*tolylurethane* melts at 123°.

5-*Bromo*-3-*nitro*-p-*tolyl ethyl carbonate* melts at 84—85°. The *hydrochloride* of 5-*bromo*-3-*amino*-p-*tolyl ethyl carbonate* melts and decomposes at 142—143° and is insoluble in water. 5-*Bromo*-4-*hydroxy*-m-*tolylurethane* melts at 83° and is soluble in alcohol or ether.

4-*Chloro*-2-*nitrophenyl acetate*, $NO_2 \cdot C_6H_3Cl \cdot OAc$, obtained by the action of acetic anhydride on 4-chloro-2-nitrophenol, melts at 47—48° and is readily soluble in benzene, chloroform, or ether, and fairly so in alcohol. On reduction with tin and hydrochloric acid, it is converted into the *hydrochloride* of 4-chloro-2-aminophenyl acetate, which melts at 105—107°; the *platinichloride* darkens at 120° and remains unmelted at 200°. 4-*Chloro*-2-*aminophenyl acetate*, $NH_2 \cdot C_6H_3Cl \cdot OAc$, crystallises in white needles and melts at 73—74°; if left for a day, it undergoes molecular rearrangement with formation of *acetyl*-4-*chloro*-2-*aminophenol*, $NHAc \cdot C_6H_3Cl \cdot OH$, which melts at 176° and may also be prepared by the action of acetic anhydride on 4-chloro-2-aminophenol. When acetyl-4-chloro-2-aminophenol is heated at 220°, it is converted into 4-chloro-2-ethenylaminophenol,

$$C_6H_3Cl{<}^{O}_{N}{\geqslant}CMe,$$

which crystallises in white needles, melts at 53—54°, has a peculiar, pleasant odour, and is soluble in ether, alcohol, benzene, or chloroform; its *hydrochloride* melts at 129—130·5°; the *platinichloride* is also described. E. G.

Molecular Transformation of Acylated Aminohydroxy-compounds. Karl Auwers (*Annalen*, 1904, **332**, 159—213).—In the course of an investigation of the phenol bromides, it was observed that when bases acted on acetyl derivatives of phenols of the type $C_6X_4(OAc) \cdot CH_2Br$, the acetyl and the substituted methyl groups being in the ortho-position relative to one another, the bromine atom was not only replaced by the base, but the acetyl group wandered from the oxygen to the nitrogen, thus:

$$OAc \cdot C_6H_2Br_2 \cdot CH_2Br + NH_2Ph \longrightarrow OH \cdot C_6H_2Br_2 \cdot CH_2 \cdot NPhAc,$$

a reaction which takes place in benzene solution either at 100° or at the ordinary temperature.

This change has only been observed in the case of *o*-hydroxybenzyl compounds, but not with the isomeric *m*- and *p*-derivatives. Investigation of the influence of the nature of the base or the acyl group on the tendency of the *o*-hydroxybenzyl compounds to undergo this transformation appears to show that the change is not dependent on these factors. The part played by the base was more particularly investigated; all the substituted anilines behave like aniline itself; the bases of the fatty series act in the same way, but still more readily; this increased activity is not due merely to their being stronger bases,

since the weaker bases effect a similar change. Whether the weakest bases (so far as they are still capable of being acetylated) are capable of producing the change cannot be decided, since they are not able to form condensation products with the brominated ψ-phenols. It has not been experimentally demonstrated that the acyl group should possess a certain definite degree of acid character in order that the transformation should occur; but since the course of the reaction appears to be independent of the strength of the base, and since even the radicle of carbonic acid can be made to wander from the oxygen to the nitrogen, it would seem that the transformation is independent also of the chemical nature of the acyl group. The mass (mol. volume) of the acyl group has no influence on the change.

No thorough attempt has up to the present been made to ascertain how far steric influences hinder or otherwise affect the transformation in the case of *o*-hydroxybenzyl derivatives. All experiments having as their object the isolation of the supposed primary product of the reaction $C_6X_4(OAc)\cdot CH_2\cdot NHPh$ (low temperatures being used during the whole of the operations), led to no result; in all cases, the product of the transformation was alone obtained; the *O*-ester is extremely labile, even if it is capable of existence.

Since it was possible that the esters of aliphatic amino-alcohols would behave towards bases as the esters of *o*-hydroxybenzyl derivatives, the action of aniline on the benzoate of ethylenebromohydrin was investigated; the reaction, which took place even at a high temperature, is represented thus: $CH_2Br\cdot CH_2OBz + 2NH_2Ph = NHPh\cdot CH_2\cdot CH_2\cdot OBz + NH_2Ph,HBr$; no wandering of the acyl group was detected. The *O*-esters of the amino-alcohols, which have mainly been investigated in the form of their salts, are stable and do not change when boiled with dilute acids. It has not yet been ascertained whether the *N*-ester of the amino-alcohols, which is also stable under ordinary conditions, can be transformed into the *O*-ester; nor is it known whether an amino-alcohol, in acylation, is converted first into an *O*- or an *N*-ester.

The aromatic are quite similar to the aliphatic alcohols, both *N*- and *O*-esters being capable of existence and not directly transformable the one into the other. If the formulæ of the stable *O*-ester of *o*-aminobenzylalcohol and of the unstable derivative of *o*-hydroxybenzylamine are compared, $-C(N{=})\cdot C{<\!\!\!<}CH_2\cdot O-$ and $-C(O-)\cdot C{<\!\!\!<}CH_2\cdot N{=}$, it is seen that the distance between the oxygen and nitrogen atoms is not materially different in the two compounds. The cause of the difference of behaviour is therefore not to be found in different spacial relations. It is suggested that the only grounds for the difference in stability of the *O*-esters of amino-alcohols on the one hand, and of *o*-hydroxybenzylamines on the other, are to be sought in the fact that the union of the alcoholic oxygen with the acyl group is more powerful than that of the phenolic oxygen; in the latter case, therefore, the attraction of the basic amino-group is sufficiently powerful to bring about the intramolecular change.

I. *Action of Aniline on Acetyl Derivatives of Substituted* o-, m-, *and* p-*Hydroxybenzyl Bromides.*—[With OTTO ANSELMINO and W. RICHTER.]

—The aniline (2 mols.) and the acetate (1 mol.), which was being studied, were heated together in benzene solution on the water-bath until the amount of aniline hydrobromide which separated no longer increased. The benzene was evaporated and the anilide isolated in various ways. By the behaviour of the product towards alkalis, it could generally be ascertained whether the acetyl group had wandered to the nitrogen, or the primary product could be converted into a diacetyl derivative by boiling with acetic anhydride, which is then hydrolysed, the identity of the resulting *N*-ester of the hydroxybenzylaniline with the initial product of the reaction showing that the acetyl group had migrated; finally, the constitution of the product could be demonstrated by condensing the original ψ-phenol, instead of its acetyl derivative, with aniline and then acetylating in the cold, when only the *N*-ester is formed and can be compared with the product of the reaction of the acetyl derivative with aniline.

A. *Ortho-compounds.*—The N-*acetate* of 3 : 5-*dibromo*-o-*hydroxybenzylaniline*, $OH\cdot C_6H_2Br_2\cdot CH_2\cdot NAcPh$, obtained from dibromo-*o*-acetoxybenzyl bromide and aniline by the action of acetic anhydride on dibromo-*o*-hydroxybenzylaniline in the cold or by hydrolysis with alcoholic sodium hydroxide of the diacetyl compound, crystallises in needles melting at 152°. The N-*acetate* of 2 : 3 : 4 : 5-*tetrabromo*-o-*hydroxybenzylaniline*, prepared from tetrabromo-*o*-acetoxybenzyl bromide and aniline, and also obtained by partial hydrolysis of the diacetate of tetrabromo-*o*-hydroxybenzylaniline, or by the acetylation in the cold of tetrabromo-*o*-hydroxybenzylaniline, crystallises in flattened needles or in lustrous prisms melting at 157—158°; the corresponding *phenol*, $OH\cdot C_6Br_2\cdot CH_2\cdot NHPh$, prepared by the action of aniline (2 mols.) on tetrabromo-*o*-hydroxybenzyl bromide (1 mol.) in benzene solution, forms needles which begin to decompose at 165° and are completely molten at 170°; the *diacetyl* derivative crystallises in rhombic leaflets melting at 161—162°.

The N-*monoacetate* of *tribromohydroxy*-m-*xylylenedianiline*,

$$\begin{array}{l}\mathrm{CBr{:}C(CH_2\cdot NHPh)\cdot CBr} \\ \mathrm{CBr{:}C(OH)\text{———}C\cdot CH_2\cdot NAcPh}\end{array}$$

(compare Abstr., 1900, i, 97), melts at 209°, has the constitution represented by the formula, and is formed when aniline interacts with 3 : 4 : 6-tribromo-2-acetoxy-*m*-xylylene bromide, the acetyl group wandering from the oxygen to the nitrogen. A similar change was observed when aniline acts on 3 : 5 : 6-tribromo-2-acetoxy-*p*-xylylene bromide.

B. *Meta-compounds.*—The O-*acetate* of 2 : 4 : 6-*tribromo*-m-*hydroxybenzylaniline*, $OAc\cdot C_6HBr_3\cdot CH_2\cdot NHPh$, prepared by the action of tribromo-*m*-acetoxybenzyl bromide (1 mol.) with aniline (2 mols.), forms crystals melting at 99—100°, and by hydrolysis with alcoholic potassium hydroxide is converted into *tribromo*-m-*hydroxybenzylaniline*, which crystallises in needles melting at 96°. When the latter is treated with cold acetic anhydride, the isomeric N-*acetate* is obtained, crystallising in prisms melting at 180°. The product obtained from dibromo-*m*-acetoxy-ψ-cumyl bromide and aniline is probably an *O*-acetate, since it is insoluble in alkali hydroxides.

C. *Para-compounds.*—The O-*acetate* of 3 : 6-*dibromo*-p-*hydroxy*-ψ-

cumylaniline, $OAc \cdot C \lessdot \genfrac{}{}{0pt}{}{CMe \cdot CBr}{CBr:CMe} \gtrdot C \cdot CH_2 \cdot NHPh$, prepared from the acetyl derivative of dibromo-ψ-cumenol bromide and aniline in benzene solution, melts at 120°; the N-*acetate* (m. p. 223—225°), obtained by the action of acetic anhydride on the base, is easily converted into the *diacetate* by boiling with acetic anhydride, which crystallises in needles or lustrous prisms melting at 140°; by digestion with alcoholic potassium hydroxide, the *N*-acetate is regenerated. A similar O-*acetate*, which is insoluble in alkali hydroxides, is obtained by the action of aniline on the acetyl derivative of 3 : 5 : 6-tribromo-4-hydroxy-*o*-xylylene bromide.

II. *Reaction of Dibromo*-o-*acetoxybenzyl Bromide with Primary Bases.* —[With H. Ulrich.]—The investigation of a number of primary bases, many of them with negative substituents, showed that they behaved in the same manner as aniline. The N-*acetate* of 3 : 5-*dibromo*-o-*hydroxybenzyl*-o *toluidine*, prepared from dibromo-*o*-acetoxybenzyl bromide (1 mol.) and *o*-toluidine (2 mols.) in benzene solution, crystallises in small needles melting at 115°. The corresponding *derivative* of β-naphthylamine, which was prepared in similar manner, forms small needles melting at 137°, and the N-*acetate*, obtained by the use of amylamine, in silky needles melting at 150°.

The N-*acetate* of 3 : 5-*dibromo*-o-*hydroxybenzyl*-o-*chloroaniline*, obtained by the use of *o*-chloroaniline, forms short prisms melting at 129—130°, and the corresponding *compound* from 2 : 4-dichloroaniline stellate groups of needles melting at 141·5—143·5°. The N-*acetate* of 3 : 5-*dibromo*-o-*hydroxybenzyl*-m-*nitroaniline*, prepared from dibromoacetoxybenzyl bromide and *m*-nitroaniline in alcoholic solution at 100°, forms yellow crystals melting at 158—159°, and the corresponding *compound* from *p*-nitroaniline yellow rhombohedra or prisms melting at 146°. *o*-Nitroaniline, 2 : 4-dinitroaniline, and 3-nitro-4-toluidine will not condense with the dibromoacetoxybenzyl bromide.

The N-*acetate* of 3 : 5-*dibromo*-o-*hydroxybenzyl*-5-*nitro*-o-*toluidine*, prepared in the usual manner, crystallises in lustrous needles or monoclinic prisms melting at 161—162°; the corresponding *compound* from 2-nitro-*p*-toluidine crystallises in yellow, rectangular plates melting at 179—180·5°. The N-*acetate* of 3 : 5-*dibromo*-o-*hydroxybenzyl*-o-*anisidine*, crystallises in prisms melting at 102—103°, and the *compound* from *p*-anisidine in star-shaped groups of needles melting at 114—115°. The N-*acetate* of 3 : 5-*dibromo*-o-*hydroxybenzylanthranilic acid* is obtained in the usual manner or by acetylating the base, 3 : 5-*dibromo*-o-*hydroxybenzylanthranilic acid*, which is obtained from dibromo-*o*-hydroxybenzyl bromide and anthranilic acid and forms transparent rhombohedra melting at 175—178°; the *acetate* crystallises in monoclinic prisms melting at 201—202°. The *acetate*, prepared from *m*-aminobenzoic acid, crystallises in small cubes melting at 213°. 3 : 5-*Dibromo*-o-*hydroxybenzyl*-m-*aminobenzoic acid*, prepared from *m*-aminobenzoic acid and dibromohydroxybenzyl bromide, forms crystals melting indefinitely at 167°, and on acetylation is converted into the derivative just described. *Methyl* 3 : 5-*dibromo*-o-*hydroxybenzyl*-m-*aminobenzoate*, prepared from dibromohydroxybenzyl bromide and methyl *m*-aminobenzoate, crystallises in small needles or prisms melting at 120—123°; on

acetylation, it yields the N-*acetate* of methyl dibromohydroxybenzyl-*m*-aminobenzoate, which can also be obtained from dibromohydroxybenzyl bromide and methyl *m*-aminobenzoate, and crystallises in groups of needles melting at 117—119°. The N-*acetate* of 3 : 5-*dibromohydroxybenzyl*-p-*aminobenzoic acid* crystallises in transparent cubes melting at 221—222°. The N-*acetate* of 3 : 5-*dibromohydroxybenzyl-ψ-cumidine* crystallises in needles or prisms melting at 120—121°.

III. *Migration of Heavy Acidic Radicles.*—[With E. Bergs and Fritz Winternitz.]—In the reaction of the benzoic, lauric, and palmitic esters of dibromo-*o*-hydroxybenzyl bromide with aniline, the acyl group wanders from the oxygen to the nitrogen just as the acetyl group migrates in the acetates. 3 : 5-*Dibromo*-o-*benzoxybenzyl bromide*, $OBz\cdot C_6H_2Br_2\cdot CH_2Br$, prepared by benzoylating dibromo-*o*-hydroxybenzyl bromide with benzoyl chloride, crystallises in needles melting at 119—120° and reacts with aniline (2 mols.) in ethereal solution forming the N-*benzoate* of dibromobenzylaniline, which forms scales melting at 163°. The *laurate* of 3 : 5-*dibromo*-o-*hydroxybenzyl bromide*, $CH_2Br\cdot C_6H_2Br_2\cdot O\cdot CO\cdot C_{11}H_{23}$, prepared by heating under reduced pressure mol. quantities of lauryl chloride and dibromo-*o*-hydroxybenzyl bromide, crystallises in needles melting at 60—61° and is converted by boiling with aniline into the N-*laurate* of dibromohydroxybenzylaniline, which forms white needles melting at 50—51°. The *palmitate* of dibromohydroxybenzyl bromide crystallises in white needles melting at 75°, and the N-*palmitate* of the benzylaniline, obtained from it, in needles melting at 56—57°; on boiling the latter with acetic anhydride, the *acetate*,

$$OAc\cdot C_6H_2Br_2\cdot CH_2\cdot NPh\cdot CO\cdot C_{15}H_{31},$$

is obtained in crystalline form melting at 64—65°, and readily converted by alcoholic potassium hydroxide into the N-palmitate.

Experiments on the reduction of the *o*-nitrophenyl esters of acids of heavy mol. weight, made with the object of ascertaining whether the *O*-ester was formed, or whether it changed into the *N*-ester, gave no distinct results, since in all cases mixtures, which could not be separated, were formed.

o-*Nitrophenyl laurate*, $NO_2\cdot C_6H_4\cdot O\cdot CO\cdot C_{11}H_{23}$, prepared by the interaction of mol. quantities of lauryl chloride and *o*-nitrophenol in solution in pyridine, crystallises in monoclinic prisms melting at 35—36°; the *palmitate* forms small needles melting at 51—52° and the *stearate* melts at 60—61°. The N-*lauryl* derivative of *o*-aminophenol, $OH\cdot C_6H_4\cdot NH\cdot CO\cdot C_{11}H_{23}$, prepared by the action of lauryl chloride on *o*-aminophenol in acetone solution, crystallises in leaflets of a pale rose colour, melting at 68—69°, and the corresponding *palmitate* in leaflets melting at 78—79°.

IV. *Experiments with Amino-alcohols.*—[With E. Bergs.]—The interaction of aniline and the acetate and benzoate of ethylenebromohydrin was investigated. In the case of the benzoate, even at a temperature of 140—150°, the *benzoate* of *β-hydroxyethylaniline*, $NHPh\cdot CH_2\cdot CH_2\cdot O\cdot COBz$, was quantitatively formed, no migration of the benzoyl group being observed. In the case of the acetate, on the other hand, both the bromine and the acetyl group were replaced

by anilino-groups, the acetyl derivative of symmetrical diphenyl ethylenediamine, $NHPh\cdot CH_2\cdot CH_2\cdot NAcPh$, being produced.

The *benzoate* of ethylenebromohydrin, $CH_2Br\cdot CH_2\cdot O\cdot COBz$, prepared by warming mol. quantities of ethylenebromohydrin and benzoyl chloride at 100°, is a clear liquid boiling at 147—149° under 15 mm. and at 280—285° with decomposition under the ordinary pressure; when warmed with aniline (2 mols.), it is converted into *β-benzoxyethyl-aniline*, crystallising in needles melting at 77°; the *hydrochloride* forms needles melting at 130°; the *nitroso*-derivative is a greenish-yellow oil, decomposing on warming. The *dibenzoate* of β-hydroxyethyl-aniline, $NPhBz\cdot CH_2\cdot CH_2\cdot O\cdot COBz$, prepared from the monobenzoate and benzoyl chloride, crystallises in needles melting at 91—92°, and by partial hydrolysis with alcoholic potassium hydroxide is converted into the N-*benzoate*, $NPhBz\cdot CH_2\cdot CH_2\cdot OH$, which crystallises in needles melting indefinitely at 142—146°. This compound could not be obtained by heating the isomeric *O*-benzoate in benzene solution at 160—180°.

When the acetate of ethylenebromohydrin is heated with aniline at 140—150°, or in benzene solution for 8—10 hours, the acetyl derivative of diphenylethylenediamine (m. p. 128°) is produced, and can be converted into the diacetyl derivative (m. p. 158°) by boiling with acetic anhydride. K. J. P. O.

Two Homologues of Catechol. RAYMOND DELANGE (*Compt. rend.*, 1904, 138, 1701—1703. Compare Abstr., 1900, i, 289).—*Ethylcatechol*, obtained from ethylcatechol methylene ether (compare Klages, this vol., i, 46) by converting it into ethylcatechol dichloromethylene ether, $CCl_2{:}O_2{:}C_6H_4Et$, boiling at 133—135° under 20 mm. pressure, by the action of phosphorus pentachloride, and boiling this compound with water, boils at 157—160° under 19 mm. pressure, is very soluble in water or the ordinary organic solvents, sparingly soluble in light petroleum (30—60°), from which it crystallises in thin needles melting at 39°. *Ethylcatechol carbonate*, $CO{:}O_2{:}C_6H_4Et$, obtained by the action of water and calcium carbonate on the foregoing *dichloro*-derivative, is a colourless, mobile liquid boiling at 135—137° under 12 mm. pressure.

iso*Propylcatechol*, $CHMe_2\cdot C_6H_3(OH)_2$, prepared by distilling *iso*propylveratrole (compare Béhal and Tiffeneau, *Bull. Soc. chim.*, 1903, 29, 1108) with a solution of hydriodic acid, boils at 167—169° under 26 mm., or at 270—272° under the ordinary pressure, crystallises from light petroleum (30—60°) in plates melting at 78°, and is also prepared similarly to the preceding compound by treating *iso*propylcatechol methylene ether (*loc. cit.*) with phosphorus pentachloride, whereby it is converted into iso*propylcatechol dichloromethylene ether*,

$$CHMe_2\cdot C_6H_4{:}O_2{:}CCl_2,$$

boiling at 131—134° under 12 mm. pressure, and decomposed by boiling with water, forming *iso*propylcatechol.

iso*Propylcatechol carbonate*, $CHMe_2\cdot C_6H_4{:}O_2{:}CO$, prepared similarly to the corresponding ethyl compound, boils at 135—137° under 13 mm.

pressure and crystallises in leafy needles melting at 41°, readily soluble in the ordinary organic solvents. M. A. W.

Constitution of Parsley-apiole and Dill-apiole. HERMANN THOMS (*Arch. Pharm.*, 1904, **242**, 344—347).—Parsley-apiole has been shown to be 2 : 5-dimethoxy-3 : 4-methyleneoxy-1-allylbenzene (*Ber.*, 1903, **36**, 1714). In a similar manner, dill-apiole has now been shown to be 5 : 6-dimethoxy-3 : 4-methyleneoxy-1-allylbenzene :

$$\begin{array}{l} CH_2{:}CH{\cdot}CH_2{\cdot}C\text{—}C(OMe){:}C{\cdot}O \\ \qquad\qquad\quad\;\; CH{\cdot}C(OMe){:}C{\cdot}O \end{array}\!\!>CH_2$$

Parsley-apiole.

$$\begin{array}{l} CH_2{:}CH{\cdot}CH_2{\cdot}C\text{———}CH{=\!=}C{\cdot}O \\ \qquad\qquad\quad\;\; C(OMe){\cdot}C(OMe){:}C{\cdot}O \end{array}\!\!>CH_2$$

Dill-apiole.

C. F. B.

Some Phenolic Ethers containing the *pseudo*-Allyl Chain, $R{\cdot}CMe{:}CH_2$. AUGUSTE BÉHAL and MARC TIFFENEAU (*Compt. rend.*, 1904, **139**, 139—141).—By the action of magnesium methiodide on cyclic alkyl esters, tertiary alcohols of the type $CRMe_2{\cdot}OH$ can be prepared; m-*methoxyphenyldimethylcarbinol*, $OMe{\cdot}C_6H_4{\cdot}CMe_2{\cdot}OH$, melts at 34°, and *veratryldimethylcarbinol*, $C_6H_3(OMe)_2{\cdot}CMe_2{\cdot}OH$, melts at 78°. In addition to the tertiary alcohol, the *pseudo*-propenyl derivative, $RCMe{:}CH_2$, is also formed, and in the presence of excess of magnesium methiodide forms the sole product (compare Abstr., 1901, i, 246, 272), and the following ψ-allyl derivatives of phenolic ethers have been thus prepared: o-ψ-*propenylanisole* boils at 198—199°, has a sp. gr. 0·983 at 21°, and n_D 1·5315; m-ψ-*propenylanisole* boils at 215—216°, has a sp. gr. 1·009 at 0°, and n_D 1·5417; 1-ψ-*propenyl*-3 : 4-*guaiacol* boils at 257—258°, has a sp. gr. 1·0832 at 15°, and n_D 1·5595; 1-ψ-*propenyl*-3 : 4-*veratrole* boils at 253—254°, has a sp. gr. 1·051 at 15°, and n_D 1·5560; 1-ψ-*propenyl*-3 : 4-*catechol methylene ether* boils at 238—239°, has a sp. gr. 1·124 at 15°, and n_D 1·5619. The physical properties of the *pseudo*-propenyl derivatives of the phenolic ethers are intermediate between those of the corresponding propenyl and *iso*propenyl derivatives. M. A. W.

Syntheses by means of Sodium Phenyl and of Magnesium Alkyl Bromides. SALOMON F. ACREE (*Ber.*, 1904, **37**, 2753—2764).—The syntheses previously effected by means of sodium phenyl (bromobenzene and sodium) can be more advantageously carried out by using magnesium phenyl bromide, and a number of syntheses of this kind are described, including that of triphenylcarbinol from benzophenone and magnesium phenyl bromide, and diphenyl α-naphthylcarbinol, $C_{10}H_7{\cdot}CPh_2{\cdot}OH$, from benzophenone and magnesium α-naphthyl bromide, or from phenyl-α-naphthylketone and magnesium phenyl bromide, and of phenyl-α-naphthylcarbinol, $C_{10}H_7{\cdot}CHPh{\cdot}OH$, from benzaldehyde and magnesium α-naphthyl bromide.

as-*Phenyl-α-naphthylethylene*, $C_{10}H_7\cdot CPh{:}CH_2$, prepared by the action of magnesium methyl iodide on phenyl α-naphthyl ketone, boils at 350—355°, crystallises from alcohol, and melts at 60°. The *bromo-derivative*, $C_{10}H_7\cdot CPh{:}CHBr$, prepared by the direct action of bromine on the hydrocarbon dissolved in chloroform, is an oil which distils at 240—260° under 15 mm. pressure.

When sodium is allowed to act on magnesium phenyl bromide, the products are diphenyl and triphenylcarbinol.

Phenylbenzoin, $OH\cdot CPh_2\cdot COPh$, is formed by the action of magnesium phenyl bromide on benzil, and is converted by the further action of magnesium phenyl bromide into benzopinacone,

$$HO\cdot CPh_2\cdot CPh_2\cdot OH.$$

α-*Naphthylbenzoin*, $C_{10}H_7\cdot CPh(OH)\cdot COPh$, prepared by the action of magnesium α-naphthyl bromide on benzil, crystallises from alcohol and melts at 132—133°.

When magnesium phenyl bromide is allowed to act on methyl benzilate, the product is benzopinacone. s-*Diphenyldi*-p-*tolylpinacone*, $C_6H_4Me\cdot CPh(OH)\cdot CPh(OH)\cdot C_6H_4Me$, prepared by a similar method, crystallises from alcohol and melts at 163—164°.

Triphenylethylene glycol, $HO\cdot CPh_2\cdot CHPh\cdot OH$, can be prepared by the action of magnesium phenyl bromide on benzoin or on methyl mandelate. *Diphenyl*-p-*tolylglycol*, $C_6H_4Me\cdot CPh(OH)\cdot CHPh\cdot OH$, prepared by the action of magnesium *p*-tolyl bromide on benzoin, crystallises from alcohol and melts at 168°. *Diphenyl-α-naphthylglycol* crystallises from alcohol and melts at 198°. T. M. L.

Methylpiperonyl Ether. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 717—723. Compare this vol., i, 668).—The substance melting at 111° (*loc. cit.*) obtained by the interaction of piperonaldehyde and magnesium methyl iodide is now found to be more readily prepared by the etherification of methylpiperonyl alcohol by inorganic salts, and to consist of methylpiperonyl ether,

$$\left(CH_2{<}\begin{matrix}O\cdot C\cdot CH{:}CH\\ O\cdot C\cdot CH{:}C\cdot CHMe\end{matrix}\right)_2 O.$$

It crystallises from alcohol or benzene in shining, rectangular prisms united in groups often 2 cm. long and 5 mm. broad; it is soluble in chloroform and to a lesser extent in ether or acetic acid. It does not decolorise a chloroform solution of bromine, combine with phenylhydrazine, hydroxylamine, or benzoyl chloride, or reduce ammoniacal silver nitrate solution, but it reduces Fehling's solution slightly. With cold sulphuric acid, it yields a bright red solution which gradually deposits violet flocks. With concentrated nitric acid, even at 0°, it gives a mixture of various nitro-derivatives. On heating, it first yields methylenedioxystyrene and methylpiperonyl alcohol:

$$(CH_2{:}O_2{:}C_6H_3\cdot CHMe)_2O = CH_2{:}O_2{:}C_6H_3\cdot CH{:}CH_2 + CH_2{:}O_2{:}C_6H_3\cdot CHMe\cdot OH;$$

the latter then decomposes, giving another molecule of methylenedioxystyrene: $CH_2{:}O_2{:}C_6H_3\cdot CHMe\cdot OH = H_2O + CH_2{:}O_2{:}C_6H_3\cdot CH{:}CH_2$.

By a few salts of the heavy metals at the ordinary temperature and at 100° by most of them or by salts of the alkali or alkaline-earth metals, methylpiperonyl alcohol is converted into methylenedioxy-

styrene, a change also brought about by the action of heat; at the ordinary temperature, it is transformed into methylpiperonyl ether if it is contaminated with traces of salts of the alkali or alkaline-earth metals remaining after its extraction. T. H. P.

Diethylanthranilic Acid. HANS MEYER (*Monatsh.*, 1904, **25**, 487—490. Compare Abstr., 1901, i, 190; Willstätter and Kahn, this vol., i, 235).—The action of ethyl iodide on anthranilic acid leads to the formation of *diethylanthranilic acid*, $NEt_2{\cdot}C_6H_4{\cdot}CO_2H$, which separates from acetic anhydride in glistening crystals, melts at 120—121°, and is neutral to potassium hydroxide and phenolphthalein. The *hydriodide* melts and decomposes at 160°; the *periodide* forms dark violet crystals; the hydrochloride melts and decomposes at 172°. The hydrochloride and the iodide are decomposed by silver oxide; with potassium hydroxide, they form *potassium* salts, for instance, $CO_2K{\cdot}C_6H_4{\cdot}NHEt_2I$. The successive action of thionyl chloride and alcohol on the acid leads to the formation of the *hydrochloride* of the ester, from which the ester is liberated by dilute sodium carbonate solution. G. Y.

Condensation of Aldehydes and Lactones with Dibasic Acids. RUDOLPH FITTIG (*Annalen*, 1904, **331**, 151—196; Abstr., 1890, 583).—I. *Condensation of Cinnamaldehyde with Succinic Acid.*—[With LUDWIG BATT.]—In continuation of earlier investigations (*loc. cit.*) the behaviour of cinnamaldehyde towards sodium succinate in the presence of acetic anhydride has been studied. Paraconic acid was not produced, but cinnamenyl*iso*crotonic acid, the sodium salt of which condenses at the same time with 2 mols. of cinnamaldehyde, water and carbon dioxide being eliminated, forming the hydrocarbon, *αθ-diphenyldibutadiene*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CHPh$. At a higher temperature, the anhydride of dicinnamylidenesuccinic acid, $\begin{array}{l} CHPh{:}CH{:}CH{:}CH{\cdot}C{\cdot}CO \\ CHPh{:}CH{\cdot}CH{:}CH{\cdot}C{\cdot}CO \end{array}\!\!>\!O$, together with a small amount of the unsaturated acid, is formed.

Molecular proportions of cinnamaldehyde, acetic anhydride, and dry sodium succinate are heated together for 20 hours at 90°; the product is treated with aqueous sodium carbonate and the mixture extracted with ether, when diphenyldibutadiene separates between the aqueous and ethereal layers; it crystallises in golden-yellow leaflets from acetic acid, melting and decomposing at 225°. When brominated in suspension in chloroform, a crystalline *tetrabromide*, which melts and decomposes at 185°, and an insoluble crystalline *octobromide*, melting and decomposing at 248°, are obtained. *Cinnamenyl*iso*crotonic acid*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$, is contained in the alkaline aqueous extract of the reaction product, and is separated from the cinnamic acid by fractional crystallisation of their calcium salts; it crystallises in leaflets melting at 111—112°; the *silver* salt is a curdy precipitate, and the *calcium* and *barium* salts crystallise with $2H_2O$. On reduction with sodium amalgam, *hydrocinnamenyl*iso*crotonic acid*,

$CH_2Ph\cdot CH\colon CH\cdot CH_2\cdot CH_2\cdot CO_2H$, is formed and crystallises in needles melting at 88°; the *silver* salt is a white precipitate, and the *barium* salt crystallises with $2H_2O$. This acid yields a *dibromide* which forms crystals melting and decomposing at 103—104°.

When the mixture above mentioned is heated for the same time at 130° and then treated with aqueous alkali, the *anhydride* of dicinnamenylidenesuccinic acid separates between the aqueous and ethereal layers; it crystallises in red needles or leaflets melting and decomposing at 215°. It is converted into the *acid* by heating with aqueous sodium hydroxide; the latter is a white, amorphous powder, which, on suddenly heating or on warming with acetic anhydride, is converted into the red anhydride. The *silver* salt is a yellow precipitate, and the *calcium* and *barium* salts are yellow powders crystallising with $4H_2O$. On reduction, *hydrodicinnamylidenesuccinic acid*, $C_8H_6Ph_2(CO_2H)_2$, is obtained, crystallising in needles melting at 182°; the *silver* salt is a white precipitate, and the *barium* salt is a crystalline powder. The *tetrabromide* crystallises in needles melting at 201°. When heated a few degrees above its melting point, hydrocinnamylidenesuccinic acid is converted into its *anhydride*, which crystallises in needles melting at 164°.

II. *Condensation of Benzaldehyde with Itaconic Acid.*—[With KARL BOCK.]—Benzaldehyde and sodium itaconate either do not react in the presence of acetic anhydride, or form a tarry mass; when the condensation is effected by Claisen's method, two stereoisomeric *dilactones*, $\begin{array}{l} O\text{——}CO\text{——}CH\text{——}CHPh \\ |\qquad\qquad\quad\ |\qquad\quad | \\ CHPh\cdot CH\colon C\cdot CO\cdot O \end{array}$, are formed; they are probably produced by the condensation of benzaldehyde with a lactonic acid, $\begin{array}{l} CH_2\colon C\cdot CH(CO_2H)\cdot CHPh \\ \qquad\ \ |\qquad\qquad\qquad\ \ | \\ \qquad CO\text{————}O \end{array}$.

A mixture of ethyl itaconate (1 mol.) and benzaldehyde (2 mols.) is slowly added to a suspension of sodium ethoxide in ether, and the mixture kept for 2 days, when it is treated with ice-water and an aqueous solution of alkali, and then extracted with ether to remove by-products; after acidification, a mixture of the two lactones separates, from which iso*diphenylheptenedilactone* is obtained, by treatment with ether, as a white solid, crystallising in needles melting at 234° and less soluble than the isomeride. The *diphenylheptenedilactone*, $C_{19}H_{14}O_4$, is soluble in the ether, from which it separates in needles (m. p. 161°); it is very readily converted into *hydroxydiphenylheptenelactonic acid*, the *barium* salt of which, $(C_{19}H_{15}O_5)_2Ba,H_2O$, forms prismatic plates and the *silver* salt a crystalline powder. The *dibasic dihydroxy-acid* forms crystalline *barium*, $C_{19}H_{16}O_6Ba$, and *calcium* salts, and an amorphous, insoluble *silver* salt. Neither the hydroxylactonic nor the dihydroxy-acid could be prepared. The *iso*dilactone forms crystalline *barium* and *calcium* salts and an amorphous *silver* salt, and can be quantitatively converted into the isomeride by boiling with bases; the reverse change could not be effected. All attempts to decompose the dilactones into benzaldehyde and the lactonic acid above mentioned were unsuccessful.

When treated with bromine in suspension in chloroform, both

dilactones yield a *diphenyldibromoheptodilactone*, $C_{19}H_{14}O_4Br_2$, which crystallises in colourless leaflets melting at 192°, and with hydrobromic acid in acetic acid solution a *diphenylbromoheptodilactone*, $C_{19}H_{15}O_4Br$, crystallising in colourless needles melting at 186°. When treated with dilute sodium hydroxide, both bromo-compounds dissolve, and on acidification yield diphenylheptenedilactone (m. p. 161°).

On reducing either of the lactones in alkaline solution with sodium amalgam, or by similar treatment of the bromo-compounds, *diphenylheptodilactone*, $C_{19}H_{16}O_4$, is formed, crystallising in needles melting at 149°, and decomposing at 157°. When treated with cold aqueous alkali, only one lactone ring is broken, salts of the monobasic hydroxy-acid being obtained; the *barium* salt, $(C_{19}H_{17}O_5)_2Ba$, and the *silver* salt both being crystalline. The corresponding dihydroxy-dibasic acid forms sparingly soluble *barium*, $(C_{19}H_{18}O_6)Ba$, *calcium*, and *silver* salts. Neither of the acids could be isolated.

III. *Condensation of Valerolactone with Succinic Acid.*—[With HARRY SALOMON and GEORG WERNHER.]—When ethyl succinate and valerolactone are heated with sodium ethoxide and the product treated with aqueous alkali, extracted with chloroform to remove neutral substances, acidified with hydrochloric acid, and again extracted with chloroform, an oil is obtained; on boiling this oil with water and removing from the aqueous liquor by ether any material soluble in that solvent, *valactenesuccinic anhydride*, $\begin{array}{l}CH_2\text{——}CH_2\quad CH_2\cdot CO\\ |\qquad\qquad\ \ |\qquad\quad |\\ CHMe\cdot O\cdot C\text{==}C\text{——}CO\end{array}\!\!>O$, remains in aqueous solution; it crystallises in needles melting at 182°. When treated with bases, the salts of valactenesuccinic acid (which has not been isolated) are obtained; the *barium* and *calcium* salts are crystalline and the *silver* salt amorphous.

The ethereal extract mentioned above contains a neutral substance melting at 155°. The alkaline extract of the original oil contains an acid which can be purified by distillation under reduced pressure; *valactenepropionic acid*, $\begin{array}{l}CH_2\cdot CH_2\\ |\\ CHMe\cdot O\end{array}\!\!>C\!:\!CH\cdot CH_2\cdot CO_2H$, is a colourless, mobile liquid boiling at 143·5—144° under 30 mm. pressure, and boiling and decomposing at 253—255° under 60 mm. pressure. The *barium*, *calcium*, and *silver* salts are amorphous and unstable.

K. J. P. O.

Isomeric Esters of *o*-Aldehydo-acids. HANS MEYER (*Monatsh.*, 1904, **25**, 491—499).—The successive action of thionyl chloride and methyl alcohol on mucobromic acid leads to the formation of a mixture of the n-*ester*, which is an oil and boils at 230—234°, and the ψ-ester, which is a hard, white, crystalline substance and boils at 249—251° (Simonis, Abstr., 1901, i, 268).

When acted upon by thionyl chloride and the product treated with methyl or ethyl alcohol, aldehydophthalic acid yields the normal esters.

Methyl aldehydophthalate, $COH\cdot C_6H_4\cdot CO_2Me$, is a colourless oil, which boils at 220—222°. It is also obtained when the acid is boiled with methyl alcohol and sulphuric acid. The ψ-methyl ester, which is

formed when the acid is boiled with methyl alcohol, boils at 242—245°.

Ethyl aldehydophthalate is a colourless oil, which boils with slight decomposition at 240—243°. When boiled with ethyl alcohol and sulphuric acid, aldehydophthalic acid forms the ψ-ester.

These normal esters of aldehydophthalic acid were previously obtained, but not purified, by Stabil (see Wegscheider, Dúbrav, and Rušnov, this vol., i, 59).

In the action of thionyl chloride on aldehydophthalic acid, Stabil's anhydride melting at 202—210° is obtained as a by-product.

G. Y.

o-**Benzoylbenzoic Acid.** HANS MEYER (*Monatsh.*, 1904, **25**, 475—486. Compare Haller and Guyot, Abstr., 1900, i, 170; 1901, i, 146).—If *o*-benzoylbenzoic acid is converted into its chloride by the action of thionyl chloride at 30—35° or of phosphorus pentachloride at 40°, the excess of reagent rapidly evaporated off under reduced pressure, and the product treated immediately with methyl alcohol, the *methyl* ester obtained crystallises in monoclinic prisms, melts at 80—81°, boils at 345—348°, and is easily soluble in alcohol, ether, acetone, or chloroform, and dissolves in sulphuric acid to a lemon-yellow solution. The action of methyl sulphate on sodium *o*-benzoylbenzoate, of methyl alcohol and concentrated sulphuric acid on the acid, or of methyl iodide on the dry silver salt leads to the formation of the methyl ester, which melts at 52° and boils at 350—352°. It dissolves in concentrated sulphuric acid to a colourless solution, which becomes yellow after some hours.

The author discusses the constitution of the isomeric methyl esters.

G. Y.

Esterification of Benzilic and Mandelic Acids. SALOMON F. ACREE (*Ber.*, 1904, **37**, 2764—2768).—n-*Propyl benzilate*,

$$HO\cdot CPh_2\cdot CO_2Pr,$$

boils at about 220° under 35 mm. pressure. iso*Amyl benzilate* boils at 230—232° under 26 mm. pressure.

T. M. L.

1:5-Diketones. II. PAUL RABE (*Annalen*, 1904, **332**, 1—21. Compare Abstr., 1902, i, 709).—Knoevenagel's views (Abstr., 1903, i, 636) as to the impossibility of distinguishing between the 1 : 5-diketones, the *cyclo*hexendiones, and the cyclic ketonic alcohols, *cyclo*hexanolones, are criticised. After a discussion of the facts which are known at present, it is concluded that these two classes of compounds, although nearly related, can be sharply distinguished by the following reactions: (i) they behave differently towards such reagents as sodium ethoxide, ammonia, and substituted ammonias, (ii) in many cases, two structural (but desmotropic) isomerides have been isolated, (iii) the condensation processes in which they are formed can be shown to consist of two phases, namely, the formation of the 1 : 5-diketone and the transformation of this compound into the cyclic compound under the influence of such bases as piperidine; the base is not necessary to the preliminary condensation, but only to the subsequent isomeric change. Thus, formaldehyde and ethyl acetoacetate in

the absence of any base (compare Knoevenagel, Abstr., 1895, i, 48) condense to form ethyl methylenebisacetoacetate,

$$CH_2(CHAc{\cdot}CO_2Et)_2,$$

an oil, which, in the presence of piperidine, passes into *ethyl* 4-*hydroxy*-4-*methyl*cyclo*hexan*-6-*one*-1 : 3-*dicarboxylate*,

$$CH_2{<}{\begin{matrix}CO\text{———}CH(CO_2Et)\\CMe(OH){\cdot}CH(CO_2Et)\end{matrix}}{>}CH_2,$$

a solid, which can be converted by way of the sodium salt into the liquid dienolic form, $CH_2{<}{\begin{matrix}C(OH){=\!=\!=}C(CO_2Et)\\CMe(OH){\cdot}CH(CO_2Et)\end{matrix}}{>}CH_2$, which slowly changes, on keeping, into the solid keto-enolic form.

Condensation Products from Ethyl Acetoacetate and Formaldehyde.—[With F. Rahm.]—When ethyl acetoacetate (2 mols.) and formaldehyde (1 mol.) are brought together in aqueous alcoholic solution, a very pure specimen of ethyl methylenebisacetoacetate is obtained, but the best yield is found when a large excess of the aldehyde is used. The product thus obtained boils at 215—218° under 35—37 mm. pressure, and gives a wine-red coloration with an alcoholic solution of ferric chloride. On treating the ester (1 mol.) in aqueous alcoholic solution at the ordinary temperature with hydroxylamine hydrochloride (2 mols.), 4-*methylenebis*-3-*methyl*-5-iso*oxazolone*,

$$\left[{\begin{matrix}N\!:\!CMe\\|\quad\\O\text{—}CO\end{matrix}}{>}CH\right]_2CH_2,$$

separates in colourless needles melting and decomposing at 180—183°; it has an acid reaction and is soluble in alkalis, but only with difficulty in acids.

The ester of the cyclic ketone-alcohol, *ethyl* 4-*hydroxy*-4-*methyl*cyclo*hexan*-6-*one*-1 : 3-*dicarboxylate*, is most readily prepared by adding piperidine directly to a mixture of paraformaldehyde and ethyl acetoacetate, cooling, and at the same time removing water by the addition of anhydrous sodium sulphate; the ester crystallises in prismatic needles melting indefinitely at 79°; in alcoholic solution, a partial change into the enolic form rapidly takes place. The *sodium* salt, $C_{13}H_{19}O_6Na$, prepared by the action of sodium on an ethereal solution of the solid ester, is a yellow, hygroscopic powder, from which, by treatment with ice-cold sulphuric acid and ether, the liquid ester of the dienolic form can be obtained; it is a yellow, very viscous oil, giving in alcoholic solution an intense violet reaction and changing gradually into the solid keto-enolic form.

Ethyl hydroxymethyl*cyclo*hexanonedicarboxylate and hydrazine hydrate yield a *pyrazolone* derivative,

$${\begin{matrix}CMe(OH)\text{—}CH_2{\cdot}C{=\!=\!=}N\\CH(CO_2Et){\cdot}CH_2{\cdot}CH{\cdot}CO\end{matrix}}{>}NH,$$

whether the keto-enolic or the dienolic ester is used; it forms prismatic crystals with a double melting point, 188° and 203°, and is soluble both in acids and alkalis. Ammonia gives, with both the esters, *ethyl* 6-*imino*-4-*hydroxy*-4-*methyl*cyclo*hexane*-1 : 3-*dicarboxylate*, $CH_2{<}{\begin{matrix}C(:NH)\text{—}CH(CO_2Et)\\CMe(OH){\cdot}CH(CO_2Et)\end{matrix}}{>}CH_2$, which separates in white needles melting at 92°.

Ethyl Ethylidenebisacetoacetate and Methylenebisacetylacetone.—[With F. ELZE.]—Whilst the true 1 : 5-diketones behave towards ammonia and its derivatives in the normal manner, the condensation product of acetaldehyde and ethyl acetoacetate, which contains ethyl ethylidenebisacetoacetate, gives, with hydroxylamine hydrochloride, a bis*iso*oxazolone, and, with ammonia, ethyl dihydrocollidinedicarboxylate. When the crude oily ethyl ethylidenebisacetoacetate is kept in solution in alcoholic ammonia for several days and the solvent then evaporated, ethyl iminohydroxydimethyl*cyclo*hexanedicarboxylate and ethyl dihydrocollidinedicarboxylate (m. p. 131°) are formed. From a solution containing the same crude ester and hydroxylamine hydrochloride, *4-ethylidenebis-3-methyl-5-isooxazolone*,

$$\left[\begin{matrix}N{:}CMe \\ | \\ O{-}{-}CO\end{matrix}\!\!>CH\right]_2CHMe,$$

separates in prismatic needles melting and decomposing at 157° and readily soluble in alkalis and acids.

When acetylacetone and formaldehyde condense in aqueous solution, besides the oily methylenebisacetylacetone, a solid *compound*, $C_{11}H_{16}O_4$, melting at 79°, and a *compound*, $C_{17}H_{24}O_6$, melting at 181°, are formed. Methylenebisacetylacetone and hydroxylamine hydrochloride give 4-methylenebis-3 : 5-dimethyl*iso*oxazole, melting at 141—142° (compare Knoevenagel, Abstr., 1903, i, 637). K. J. P. O.

Explanation of Tautomeric Phenomena. II. Desmotropic-isomeric Cyclic β-Ketonic Esters. PAUL RABE and ADOLF BILLMANN (*Annalen*, 1904, 332, 22—37. Compare preceding abstract, and Abstr., 1901, i, 33).—As a continuation of earlier investigations of tautomeric phenomena (*loc. cit.*), it has been ascertained that the desmotropic-isomeric forms of ethyl 4-hydroxy-2 : 4-dimethyl*cyclo*hexane-6-one-1 : 3-dicarboxylate, ethyl 4-hydroxy-2-*p*-nitrophenyl-4-methyl*cyclo*hexane-6-one-1 : 3-dicarboxylate, and of ethyl 4-hydroxy-2-*m*-nitrophenyl-4-methyl*cyclo*hexan-6-one-1 : 3-dicarboxylate pass readily, one into the other. The molten ketonic or enolic forms or the solutions of these forms always undergo change, a mixture of the two forms resulting. In some cases, when the ketonic form is insoluble and has a high melting point, this form separates in the solid state from such liquid mixtures or from the solutions. Besides existing in ketonic and enolic forms, the 5-*p*-nitrophenyl ester is found in two stereoisomeric modifications, a phenomenon not hitherto observed in cyclic β-ketonic esters.

The keto-form of ethyl 4-hydroxy-2 : 4-dimethyl*cyclo*hexan-6-one-1 : 3-dicarboxylate, $CH_2\!<\!\begin{matrix}CO{\text{———}}CH(CO_2Et) \\ CMe(OH){\cdot}CH(CO_2Et)\end{matrix}\!>\!CHMe$ (the "β-ester"), has already been described by Knoevenagel (Abstr., 1895, i, 48); it melts at 80°, gives no coloration with ferric chloride, and slowly decomposes into a viscous oil. The *sodium* salt of the enolic ester (the "α-ester"), $C_{14}H_{21}O_6Na,EtOH$, is prepared by adding sodium (1 atom) to a solution in absolute alcohol of the keto-ester (1 mol.); it forms white, hygroscopic crystals melting at 75—78°, and decomposes on keeping. The *enolic* ester (Abstr., 1899, i, 239) prepared from the

sodium salt melts at 60—63° and immediately begins to change into the keto-form.

Whilst Knoevenagel and Hoffmann (Abstr., 1899, i, 116, 214) obtained from ethyl acetoacetate and *p*-nitrobenzaldehyde one ester (m. p. 170—171°), "ethyl *p*-nitrobenzylidenebisacetoacetate," two stereoisomeric cyclic *ketonic esters*,

$$CH_2<\begin{matrix}CO\text{———}CH(CO_2Et)\\CMe(OH)\cdot CH(CO_2Et)\end{matrix}>CH\cdot C_6H_4NO_2,$$

the β_1- and β_2-esters, have now been isolated by fractional crystallisation from alcohol; the β_1-*ester* crystallises in needles melting at 164° and is doubtlessly identical with Knoevenagel's compound (m. p. 171°); it yields the *sodium* salt of the α_1-ester, $C_{19}H_{22}O_8NNa$, which melts at 152° and is hydrolytically dissociated in water, part of the ester changing into the β_1-ester, which then crystallises out. The α_1-*ester* is prepared from the sodium salt by treatment with dilute sulphuric acid and ice, and crystallises in rhombic leaflets melting at 129—130°; it is very stable, has a marked acid character, and gives with ferric chloride an intense violet coloration, but partially changes into the β_1-form when molten; it is more soluble than the β_1-form.

The β_2-*ester*, which is more soluble than the β_1-ester, crystallises in rhombic leaflets melting at 152—153°, and can be converted into the corresponding enolic form, the α_2-*ester*, by way of the sodium salt; this enolic form forms prismatic crystals, melting at 130—135°, when it partially passes into the keto-form. In the molten state or in solution these four isomeric esters are unstable and in time yield an allelotropic mixture.

The β-ester, the ketonic form, of ethyl 4-hydroxy-2-*m*-nitrophenyl-4-methyl*cyclo*hexane-6-one-dicarboxylate was prepared according to Knoevenagel's method (*loc. cit.*) and crystallises in slender, prismatic needles melting at 146°, when it partly changes into the enolic form. The *sodium* salt of the enolic form, the α-ester, $C_{19}H_{22}O_8NNa,EtOH$, prepared in the usual way, forms lemon-yellow, hygroscopic crystals melting at 151°. The α-ester is obtained from the β-ester by dissolving the latter in alcohol, adding a concentrated solution of sodium ethoxide in alcohol, and then pouring into ice-cold dilute sulphuric acid; the α-ester forms a yellow oil, which very rapidly changes into the β-form; in alcoholic solution, it gives a violet coloration with ferric chloride.

K. J. P. O.

5-Acetylamino-2-hydroxybenzylideneacetophenone. FRANZ KUNCKELL (*Ber.*, 1904, 37, 2826—2827. Compare Abstr., 1903, i, 509).—5-*Acetylamino-2-hydroxybenzylideneacetophenone*,

$$NHAc\cdot C_6H_3(OH)\cdot CO\cdot CH\colon CHPh,$$

is formed when 5-acetylamino-2-hydroxyacetophenone is heated with benzaldehyde in alcoholic sodium hydroxide solution and the product treated with hydrochloric acid. It crystallises in yellow needles, melts at 190°, is easily soluble in aqueous alkali hydroxides or alcohol, and, when heated with acetic anhydride and sodium acetate, yields the *triacetyl* compound, $NAc_2\cdot C_6H_3(OAc)\cdot CO\cdot CH\colon CHPh$, which forms long, white needles and melts at 147°. With bromine in carbon disulphide

solution, the triacetyl compound forms a *dibromide* which melts at 170°. G. Y.

Stereoisomeric Oximes of Dypnone (Diphenyl-1-methyl-propenon-3). FERDINAND HENRICH and A. WIRTH (*Monatsh.*, 1904, 25, 423—442. Compare this vol., i, 431).—When treated with acetic anhydride and a drop of sulphuric acid, *syn*-dypnoneoxime yields an *acetyl* derivative which crystallises in stellate groups of needles, melts at 74°, is easily soluble in alcohol or ether, and is hydrolysed to the *syn*-oxime by alcoholic potassium hydroxide. With phenylcarbimide, the *syn*-oxime forms a *derivative* which separates from benzene in white crystals and melts at 149—150°. Reduction of the *syn*-oxime with sodium and amyl alcohol leads to the formation of *αβ-diphenyl-β-methylallylamine hydrochloride*, $CMePh\colon CH\cdot CHPh\cdot NH_2\cdot HCl$; the *platinichloride* is yellow, crystallises from alcohol, and melts at 198°; the *picrate* forms yellow crystals and melts at 191°. G. Y.

Influence of the Introduction of Unsaturated Radicles on the Rotatory Power of Certain Molecules. Allyl Ethers of Borneol, Menthol, β-Methyl*cyclo*hexanol, and of Linalool. ALBIN HALLER and FRANÇOIS MARCH (*Compt. rend.*, 1904, 138, 1665—1669. Compare Abstr., 1903, i, 503, 563, 628).—*Bornyl allyl ether*,

$$C_{10}H_{17}\cdot O\cdot C_3H_5,$$

obtained by the action of allyl iodide on the sodium derivative of borneol, is a liquid boiling at 105—107° under 17 mm. pressure, has a sp. gr. 0·9376 at 0°/4°, or 0·9221 at 21°/4°, molecular refraction =59·15, theoretical value 59·025, and $[\alpha]_D$ −59°6′, the rotatory power of the borneol used being $[\alpha]_D$ − 35°40′. *Menthyl allyl ether*, $C_{10}H_9\cdot O\cdot C_3H_5$, prepared similarly to the preceding compound, is a colourless liquid with a characteristic odour, boiling at 103—104° under 13 mm. pressure, has a sp. gr. 0·8830 at 0°/4°, or 0·8763 at 19°/4°, molecular refraction 61·01, theoretical value 61·127, $[\alpha]_D$ − 98°30′, whilst the menthol employed had $[\alpha]_D$ − 49°4′. *β-Methyl*cyclo*hexyl allyl ether*, $C_7H_{13}\cdot O\cdot C_3H_5$, obtained by heating the sodium derivative of β-methyl*cyclo*hexanol prepared by Kondakoff and Schindelmeiser's method (*J. pr. Chem.*, 1900, [ii], 61, 482) with allyl bromide, boils at 79—81° under 18 mm. pressure, has a sp. gr. 0·8837 at 0°/4°, or 0·8738 at 15°/4°, molecular refraction 47·58, the theoretical value being 47·31, and $[\alpha]_D$ − 14°20′. The β-methyl*cyclo*hexanol employed had $[\alpha]_D$ + 1°30′ and was not quite free from β-methyl*cyclo*hexanone. *Linalyl allyl ether*, $C_{10}H_{17}\cdot O\cdot C_3H_5$, prepared similarly to the isomeric bornyl compound, is a colourless liquid boiling at 103—105° under 15 mm. pressure, has a sp. gr. 0·8722 at 0°/4°, or 0·8665 at 16°/4°, molecular refraction 61·45, the theoretical value being 62·43, $[\alpha]_D$ + 2°2′, whilst the linalool employed had $[\alpha]_D$ − 6°20′.

With the exception of linalyl allyl ether, the allyl ethers of the alcohols examined have a higher specific rotation than the original alcohol.

Attempts to prepare the propyl ethers of the same alcohols by the action of propyl iodide on the sodium derivative of the alcohol were unsuccessful (compare Abstr., 1903, i, 503, and Hecht, Conrad, and

Brückner, Abstr., 1890, i, 4). By the action of propyl *p*-toluenesulphonate on the sodium derivative of menthol, two liquids were obtained, one, probably propyl menthyl ether, boiling at 112—114° under 19 mm. pressure, having $[\alpha]_D -43°40'$, the other boiling at 114—116° under 19 mm. pressure. M. A. W.

Terpenes and Ethereal Oils. Camphorphorone and its Decomposition. OTTO WALLACH [with FRITZ COLLMANN] (*Annalen*, 1904, 331, 318—333).—Although dihydropulegenone and dihydrocamphorphorone have been shown to be identical (Abstr., 1903, i, 567), the corresponding unsaturated ketones, $C_9H_{14}O$, pulegenone and camphorphorone, are isomeric, their relation being expressed by the formulæ $\begin{array}{l} CHMe\cdot CO \\ | \\ CH_2—CH \end{array} \!\!> CPr^{\beta}$ and $\begin{array}{l} CHMe\cdot CO \\ | \\ CH_2—CH_2 \end{array} \!\!> C{:}CMe_2$. The ready decomposition of pulegenone by acids into acetone and 1 : 2-methyl*cyclo*pentanone is not found to occur under the same conditions in the case of camphorphorone, which is only decomposed by alkaline reagents.

The yield of camphorphorone reaches a maximum of 44 per cent. when calcium camphorate, completely dried, is distilled; if the calcium salt is distilled with soda-lime, the yield falls to 24 per cent., and if the soda-lime is moist, the yield falls to 13 per cent., an increasing quantity of 1 : 2-methyl*cyclo*pentanone appearing in the distillate. The latter can be recognised and isolated as *semicarbazone*, which melts at 174—176°; 1 : 2-*methyl*cyclo*pentanone* is an oil boiling at 140—141°, which has a sp. gr. 0·917 and n_D 1·4348 at 20°; the *oxime* is a liquid boiling at 100—102° under 18 mm. pressure. When oxidised with chromic and sulphuric acids or with neutral potassium permanganate, the pentanone is easily converted into γ-acetylbutyric acid, the *semicarbazone* of which melts at 170—171°, these facts demonstrating the constitution of the pentanone.

That the methyl*cyclo*pentanone is actually formed from the camphorphorone is shown by the fact that it is produced in large quantities together with acetone when camphorphorone is dropped on molten potassium hydroxide.

Pure camphorphorone reacts more rapidly with semicarbazide acetate than does the crude material; the normal *semicarbazone* melts at 197° and readily combines with another mol. of semicarbazide, forming a *semicarbazide-semicarbazone*, which melts at 135° and is produced when camphorphorone is treated with excess of semicarbazide in acetic acid solution; it combines with picric acid forming a yellow, crystalline *compound* melting at 146—147°. Camphorphorone can only be recovered with difficulty from its semicarbazone by warming with sulphuric acid, and when purified in this manner boils at 199—201°, has a sp. gr. 0·93, and n_D 1·4897 at 20°; it shows, therefore, the optical behaviour of an alcohol with two ethylenic linkings, and thus resembles pulegone, *iso*thujone, carvenone, menthenone, &c.

Kerp and Müller (Abstr., 1898, i, 265) found that from the additive product of sulphur dioxide and camphorphorone an isomeric substance, β-camphorphorone, is obtained, to which the formula of pulegenone has been ascribed. On repeating these experiments, it was found that β-camphorphorone is nothing but camphorphorone in a very pure state;

in fact, the formation of the additive product with sulphur dioxide affords the best method of purifying camphorphorone. Pulegone behaves in the same manner towards sulphur dioxide.

The normal *oxime* of camphorphorone is prepared in the same manner as the normal compound of pulegone, and is a viscid oil which distils under reduced pressure and is volatile with steam; it is soluble in dilute acids. K. J. P. O.

Terpenes and Ethereal Oils. Additive Products of Nitrogen Trioxide and Nitrosyl Chloride with Unsaturated Compounds. OTTO WALLACH (*Annalen*, 1904, 332, 305—336).—After an historical *résumé* of recent work on the additive compounds formed by the action of nitrogen trioxide and peroxide and of nitrosyl chloride on unsaturated compounds, a method of transforming aliphatic α-ketones into β-ketones and *vice versâ* is described, thus: COPhEt $\longrightarrow$ CHPhEt·OH $\longrightarrow$ CHPh:CHMe $\longrightarrow$ $[CHPh(NO)\cdot CHMe(NO_2)]_2$ $\longrightarrow$ $CHPh:CMe\cdot NO_2$ $\longrightarrow$ $CH_2Ph\cdot CMe:NOH$ $\longrightarrow$ $CH_2Ph\cdot COMe$ (compare Abstr., 1902, i, 806, and this vol., i, 424).

Compounds of the Anethole Series.—[With HANS MÜLLER.]—Anethole nitrite (compare Wieland, this vol., i, 54) is prepared by adding a concentrated solution of sodium nitrite to a solution of sulphuric acid, on which lies a solution of anethole in petroleum. The *β-nitroanethole*, $OMe\cdot C_6H_4\cdot CH:CMe\cdot NO_2$, prepared by Tönnies' method (Abstr., 1888, 264) from the nitrite, is easily converted by digestion with hydroxylamine hydrochloride in alkaline solution into the oxime,

$$OMe\cdot C_6H_4\cdot CH:N\cdot OH,$$

which crystallises in prisms melting at 61°; its *benzoyl* derivative melted at 109°. When the β-nitroanethole is warmed with potassium carbonate alone, anisaldehyde is obtained; on treatment with hydrochloric acid, anisaldehyde and hydroxylamine are produced. On reducing the nitro-compound with zinc dust and acetic acid, an *oxime*, $OMe\cdot C_6H_4\cdot CH:CMe:N\cdot OH$, is formed, which melts at 65—66° and distils at 160—170°; the *hydrochloride* melts at 123—124°. On hydrolysing the oxime with dilute sulphuric acid and distilling the product with steam, the *ketone*, $OMe\cdot C_6H_4\cdot CH_2\cdot COMe$, is obtained as an oil boiling at 141°, and having a sp. gr. 1·07, and $[n]_D$ 1·5253 at 20°; with hydroxylamine, it yields the oxime from which it was produced, and with semicarbazide a *semicarbazone*, $C_{11}H_{15}O_2N_3$, which crystallises in leaflets melting at 175°. That the ketone is not identical with the other possible product, methoxyphenyl ethyl ketone, was shown by a comparison of the benzoyl derivatives and the semicarbazones (compare Wallach and Pond, Abstr., 1896, i, 94). Further, when oxidised with sodium hypobromite, bromoform and anisic acid together with anisylacetic acid (m. p. 85—86°) are produced.

When the stable anethole nitrosochloride is warmed with alcohol, it is converted into anisaldehyde and hydroxylamine hydrochloride. Sodium methoxide in methyl-alcoholic solution acts on the nitrosochloride, producing the *sodium* salt, $C_{11}H_{14}O_3NNa$ (crystallising in needles), of the *oxime*, $OMe\cdot C_6H_4\cdot C(NOH)\cdot CHMe\cdot OMe$, which is obtained from the sodium salt by the action of carbon dioxide; it melts at 48—49° and distils under reduced pressure at 194°. The *hydrochloride*

melts at 125°. When hydrolysed with dilute sulphuric acid at 80°, the *ketone*, $OMe\cdot C_6H_4\cdot CO\cdot CHMe\cdot OMe$, is obtained as a yellow oil distilling under reduced pressure at 160°; its *semicarbazone* melts at 192°; on oxidation with chromic acid, it is converted into anisaldehyde and acetic acid together with a little anisic acid.

Compounds of the iso*Safrole Series.*—[With HANS MÜLLER.]—By warming *iso*safrole nitrite (m. p. 128°) either with acetyl chloride or with sodium methoxide or alcoholic potassium hydroxide, *β-nitro*iso*safrole*, $CH_2:O_2:C_6H_3\cdot CH:CMe\cdot NO_2$, is obtained in yellow crystals melting at 98°; when warmed with hydroxylamine hydrochloride and sodium carbonate in alcoholic solution, it is converted into piperonaldoxime (m. p. 111°; compare Angeli, 1893, i, 261). On reduction of the nitro-compound, the *oxime*, $CH_2:O_2:C_6H_3\cdot CH_2\cdot CMe:NOH$, which melts at 86—87°, is formed, and is converted by treatment with dilute sulphuric acid into the corresponding *ketone*, boiling at 156° under reduced pressure and having a sp. gr. 1·203 and $[n]_D$ 1·5430 at 20°. The *semicarbazone* melts at 163°. When the ketone is oxidised with sodium hypobromite, piperonylic (m. p. 228°) and piperonylacetic acids (m. p. 127—128°) are formed, together with a hydroxy- or ketonic acid.

On treating the nitrosochloride of *iso*safrole with sodium methoxide, an *oxime*, $CH_2:O_2:C_6H_3\cdot C(:NOH)\cdot CHMe\cdot OMe$, is obtained, which melts at 74° and boils under reduced pressure at 200—205°; its *hydrochloride* melts at 98°; the *ketone*, prepared from the oxime by the action of dilute sulphuric acid, is a yellow oil, boiling at 173—174° under reduced pressure, which yields a *semicarbazone* melting at 181°.

*Compounds of the Methyl*iso*eugenole Series.*—[With ERICH BESCHKE.]—The nitrite of methyl*iso*eugenole is converted by alcoholic alkali hydroxide into the nitro-compound, $C_6H_3(OMe)_2\cdot CH:CHMe\cdot NO_2$, which crystallises in golden-yellow needles melting at 72°. By zinc dust and acetic acid, it is reduced to a crystalline *oxime*, which yields, on hydrolysis with dilute sulphuric acid, the *ketone*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot COMe,$$

an oil boiling at 195—200° under 11 mm. pressure and volatile in steam. The *semicarbazone* melts at 176°. The *nitrosochloride* melts and decomposes at 110°. K. J. P. O.

Terpenes and Ethereal Oils. A New Case of Optical Isomerism. OTTO WALLACH (*Annalen*, 1904, 332, 337—351).—The 1 : 3-methyl*cyclo*hexanone (this vol., i, 424) has an optical activity, which is markedly influenced by the nature of the solvent; thus, in ethyl alcohol, $[\alpha]_D$ is +10·45°; in chloroform, +14·77°; in carbon tetrachloride, +11·86°; and in ether, +17·44°. The mean value is taken as +13·38° at 15°. The oxime obtained from this dextrorotatory methyl*cyclo*hexanone is lævorotatory, having $[\alpha]_D$ −42·05° in ether at 21°. When benzoylated, this oxime yields a mixture of two *benzoyl* derivatives, which differ not only in crystalline form and melting point, but also in rotatory power; the *α-compound*, which is formed in much the larger proportion, is obtained free from the *β*-variety by repeated crystallisation from methyl alcohol and then from petroleum, and forms large, transparent, hemimorphic, monoclinic, pyroelectric crystals [$a:b:c = 0·8796 : 1 : 0·9752$; $\beta = 115°57·3'$],

melting at 96—97° and having $[\alpha]_D$ +19·97° in ethereal solution at 22°. The *β-compound* can only be prepared with difficulty, and crystallises from petroleum in thin prisms melting at 82—83°, belonging to the hemihedric rhombic system

$$[a:b:c = 0\cdot72482:1:0\cdot8641];$$

this substance is lævorotatory, having $[\alpha]_D$ −86·08° in ethereal solution at 21°.

Both benzoyl derivatives yield the pure oxime (m. p. 43—44°); since the possibility of different chemical constitutions, or of their not being true oximes, $\begin{matrix} CHMe\cdot CH_2\cdot C{:}NOBz \\ | \qquad\qquad\quad | \\ CH_2\text{——}CH_2\cdot CH_2 \end{matrix}$, but nitroso-derivatives, $\begin{matrix} CHMe\cdot CH_2\cdot CBz\cdot NO \\ | \qquad\qquad\quad | \\ CH_2\text{——}CH_2\cdot CH_2 \end{matrix}$, when a second asymmetric carbon atom would be present, seems to be excluded, the stereoisomerism must be due to the nitrogen atom, and the two varieties must be *syn-* and *anti-*forms. Up to the present, no such case has been observed in which such an isomerism has been accompanied with different optical activity.

[With W. KEMPE.]—Although the lævorotatory 1:3-methyl*cyclo*hexanone has not been prepared, the inactive modification can be obtained. When the oxime is benzoylated, two inactive modifications are formed, which can be separated by crystallising from a mixture of ethyl acetate and petroleum; the *α-compound*, which exceeds the isomeride very largely in amount, forms monoclinic crystals $[a:b:c = 0\cdot886:1:0\cdot970;\ \beta = 117°21']$ melting at 105—106°; the *β-compound* crystallises in needles melting at 70—72°.

Although stereoisomeric oximes of unsaturated cyclic ketones are known, another example of a similar phenomenon in a saturated ketone has not hitherto been observed. 1:3-Methyl*cyclo*pentanone, which is powerfully dextrorotatory, yields a mixture of oximes, from which a product (the α-oxime) crystallising in prisms (from petroleum) and melting at 91—92·5° could be isolated; from the mother liquor, no substance with a constant melting point could be obtained; both the original crystals and the substance contained in the mother (the β-oxime) liquor have $[\alpha]_D$ about +50° in ethereal solution. On benzoylating the α-oxime, melting at 91—92·5°, a feebly dextrorotatory material, which melted at 60—61°, was obtained, but the β-oxime from the mother liquor also gave a benzoyl derivative melting at 60—61°; their rotations in ether were respectively +29·77° and +34·64°.

Attempts were also made to obtain two benzoyl derivatives from *l*-menthoneoxime, but only one compound, which melted at 54° and had $[\alpha]_D$ 1·904°, was found.

K. J. P. O.

[Carone and Fenchyl Alcohol.] IWAN KONDAKOFF (*J. pr. Chem.*, 1904, [ii], 69, 566—568).—The oxidation of Nikitin's carone (*J. Russ. Phys. Chem. Soc.*, 1904, 26, [6]) by potassium permanganate was due to the presence of carvenone. Nikitin's isomeric liquid fenchyl alcohol (*loc. cit.*) is *d-l*-fenchyl alcohol containing considerable quantities of fenchone.

G. Y.

Complete Synthesis of Rhodinol, the Characteristic Alcohol of Essence of Roses. LOUIS BOUVEAULT and GOURMAND (*Compt. rend.*, 1904, 138, 1699—1701).—The authors have synthesised rhodinol, the characteristic alcohol of essence of roses (compare Bouveault and Barbier, Abstr., 1896, i, 445). By reducing ethyl geranate (compare Barbier and Bouveault, Abstr., 1896, i, 445, 637) by means of sodium and absolute alcohol (compare Abstr., 1903, i, 730), or by reducing synthetical geranic acid by sodium and amyl alcohol (compare Tiemann, Abstr., 1899, i, 190), citronellic acid,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

is obtained, which boils at 146° under 10 mm. pressure, is converted into the ethyl ester boiling at 115° under 10 mm. pressure by heating with ethyl bromide and sodium ethoxide; this, on reduction with sodium and absolute alcohol, yields inactive (racemic) rhodinol, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2OH$, boiling at 110° under 10 mm. pressure and having a sp. gr. 0·877 at 0°/4°. But for its optical inactivity, racemic rhodinol is identical with the rhodinol of essence of roses or pelargonium; its *pyruvate* is a colourless oil boiling at 143° under 10 mm. pressure, and forms a *semicarbazone* melting at 112°, soluble in methyl alcohol and sparingly so in ether (compare this vol., i, 465); the semicarbazone, similarly prepared from the active alcohol, has the same solubility and melting point and does not depress the melting point of the inactive compound. M. A. W.

Equilibrium between Chlorocamphor and Bromocamphor. MAURICE PADOA (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 723—732).—Mixtures containing from 0 to 10 per cent. of chlorocamphor have freezing points slightly higher than that of pure bromocamphor; further increase of the proportion of chlorocamphor lowers the freezing point until about 20 per cent. of the chloro-compound is present, after which the melting point curve rises continually to a maximum again.

It is found that chlorocamphor and bromocamphor are completely isodimorphous, that is, they give two distinct series of mixed crystals in all proportions, one being monoclinic and the other cubic. A triple point exists at 75·6°, at which liquid, monoclinic and cubic crystals, all containing about 40 per cent. of bromocamphor, exist together.

T. H. P.

History of the Dicyclic Thujenes. IWAN L. KONDAKOFF (*J. pr. Chem.*, 1904, [ii], 69, 560—565. Compare Abstr., 1902, i, 807; Tschugaeff, this vol., i, 515).—A criticism of Tschugaeff's work and a claim for priority. G. Y.

Matico Oil. HERMANN THOMS (*Arch. Pharm.*, 1904, 242, 328—344).—The oil examined was similar to that investigated by Fromm and van Emster (Abstr., 1903, i, 188). The matico ether of these observers was a mixture of much dill-apiole with less parsley-apiole (Ciamician and Silber, Abstr., 1888, 1100; 1896, i, 608). This mixture forms the bulk of the oil; also present are a *hydrocarbon* which boils at 121—130° under 13 mm. pressure and solidifies at −18°, and a

small amount of a *phenol ether* which yields a *bromo*-derivative melting at 123—124°. The bromo-derivative prepared from the lowest boiling fraction of the oil, which contained the least apiole, had relatively the highest melting point and percentage of bromine and the lowest percentage of methoxyl. Fromm and van Emster's maticoic acid was a mixture of parsley-apiolic acid with dill-apiolic acid ; the latter melts at 151°. There is no longer any reason to suppose that three carbon atoms are lost as a result of the bromination, the bromo-derivative not having been formed from the "matico ether" (apiole) at all, but from the phenol ether.

These results are confirmed by Fromm, who acknowledges that his matico-aldehyde must have been a mixture of dill- and parsley-apiole-aldehydes, and his homomaticoic acid a mixture of the two corresponding homo-apiolic acids, as yet unknown in the pure state. C. F. B.

Decomposition of the Colloid Molecule of Caoutchouc and its Conversion into a Cyclic Hydrocarbon. RUDOLF DITTMAR (*Monatsh.*, 1904, 25, 464—474. Compare Abstr., 1902, i, 386 ; Harries, Abstr., 1902, i, 811).—Para-rubber is best purified by successive and repeated extraction with acetone, dilute potassium hydroxide, and water. After drying over sulphuric acid, the caoutchouc is soluble in fused paraffin, hot benzaldehyde, or quinoline.

The yellow, amorphous substance formed by oxidation of caoutchouc with fuming nitric acid is probably 3 : 6- or 5 : 6-dinitrodihydrocuminic acid. It is soluble in glacial acetic acid, acetone, or quinoline. After repeated solution and reprecipitation by ether, the solubility diminishes and a brown, polymeric (?) substance, insoluble in ethyl acetate, is obtained. The *alkali* salts, $C_{10}H_{11}O_6N_2M'$, are red, amorphous substances, and are soluble in water. The *methyl* ester, $C_9H_{11}O_4N_2 \cdot CO_2Me$, formed by the action of sodium methoxide on the acid in methyl alcoholic solution, is obtained as a red powder, which, when heated, swells up like mercuric thiocyanate. The acetyl anhydride, $C_9H_{11}O_4N_2 \cdot CO \cdot OAc$, is an orange-red powder and melts at 72°.

When heated with stannous chloride and hydrochloric acid in a sealed tube at 100°, the dinitro-compound is reduced to *diaminodihydro-p-cuminic acid*, which is obtained as a dark brown powder. G. Y.

Decomposition of Paracaoutchouc by Ozone. CARL D. HARRIES (*Ber.*, 1904, 37, 2708—2711).—When a chloroform solution of paracaoutchouc is oxidised with ozone and the solvent removed, a vitreous mass is obtained which possesses all the properties of an ozonide (this vol., i, 361). It has the composition $(C_{10}H_{16}O_6)_2$ or $(C_{10}H_{16}O_6)_3$, dissolves readily in alcohol, ethyl acetate, acetic acid, or benzene, may be purified by solution in ethyl acetate and precipitation with light petroleum, and, when boiled for a short time with water, yields hydrogen peroxide and a substance which gives the reaction of a keto-aldehyde or dialdehyde (Abstr., 1898, i, 232 ; 1902, i, 345). When boiled for a longer time with water, the hydrogen peroxide oxidises the aldehydes, and from the product thus obtained lævulic acid and an *acid* melting at 195° have been isolated. Oxalic acid is not formed. The acid melting at 195° appears to be a succinic acid.

The grouping $\overset{C}{\underset{C}{}}\!\!>C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}C$ in the molecule of paracaoutchouc is suggested.

All ozonides emit rays which affect a photographic plate more readily than ozone itself. J. J. S.

Colophonia Elemi from Colophonia Mauritiana. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1904, 242, 348—351. Compare Abstr., 1902, i, 812).—The sample examined came from the Mauritius, and had acid number 36 and saponification number 63. From its solution in ether, one per cent. aqueous ammonium carbonate extracted amorphous α-iso*colelemic acid*, $C_{37}H_{56}O_4$, which melted at 120—122°. One per cent. aqueous sodium carbonate then extracted acids, from a solution of which in a mixture of methyl and ethyl alcohols *coleleminic acid*, $C_{39}H_{56}O_4$, melting at 215°, crystallised; whilst amorphous β-iso*colelemic acid*, $C_{37}H_{56}O_4$, melting at 120°, remained in solution. The remaining solution, when distilled with steam, yielded an *essential oil*, boiling chiefly at 170—175°; the residue yielded crystals of *colamyrin*, $C_{30}H_{50}O$ (which was separated by benzoylation, &c., into α- and β-amyrins), and amorphous *coleleresen*, $(C_{15}H_{24}O)_n$, melting at 75—77°. A *bitter-principle* and *bryoidin* were also present.

In 100 parts of the drug there were contained: α-*iso*colelemic acid, 10; coleleminic acid, 2; β-*iso*colelemic acid, 8; colamyrin, 25—30; coleleresen, 30—35; essential oil, 3; bitter-principle and bryoidin, traces; plant remains and impurities, about 10. C. F. B.

Tacamahaca Elemi. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1904, 242, 352—365. Compare Abstr., 1902, i, 812).—A number of samples of Tacamahaca resin were examined by moistening a little of each under the microscope with cold alcohol and noting whether or not any crystalline residue remained after the amorphous part had dissolved. One representative of each class was then examined in greater detail (compare also following abstract).

The specimen containing crystalline constituents came from the Philippines; it had acid number 35·5 and saponification number 65·2. From a solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracted amorphous α-iso*tacelemic acid*, $C_{37}H_{56}O_4$, which melts at 120—121° and yields a monopotassium salt when treated with cold potassium hydroxide solution, a dipotassium salt on heating. One per cent. aqueous sodium carbonate then extracts acids, from a solution of which *tacelemic acid*, $C_{37}H_{56}O_4$ (molecular weight determined), melting at 215°, crystallises, whilst amorphous β-iso*tacelemic acid*, $C_{37}H_{56}O_4$, melting at 120°, remains dissolved; both these acids resemble that just described in their reaction with an alkali. By distillation of the remaining solution with steam, an *essential oil* was obtained, boiling chiefly at 170—175°. From the residue, crystalline *tacamyrin*, $C_{30}H_{50}O$, was obtained; this was identical with amyrin from other sources: it melted at 170°, and its benzoyl derivative was separated into a mixture in about equal quantities of α- and β-benzoates, melting at 191—192° and 228—229° respectively, from which α- and

β-amyrins were regenerated, with melting points 181° and 192°. There remained amorphous *taceleresen*, $(C_{15}H_{24}O)_n$, melting at 75°. A *bitter-principle* is present in the resin also.

The amyrin, $C_{30}H_{50}O$, is oxidised by permanganate in glacial acetic acid to monobasic *amyrinic acid*, $C_{29}H_{47}\cdot CO_2H$ (molecular weight determined), which melts at 126—127°. From the behaviour of amyrin when oxidised (compare also Vesterberg, Abstr., 1892, 290) it is presumably a primary alcohol, $C_{29}H_{47}\cdot CH_2\cdot OH$. Taceleresen yields only oxalic and picric acids, in addition to amorphous products, when it is heated with nitric acid of sp. gr. 1·34; no camphoric or camphoronic acid is formed.

In 100 parts of the resin are contained: α-*iso*tacelemic acid, 5; tacelemic acid, 2; β-*iso*tacelemic acid, 3; essential oil, 2; tacamyrin, 30—35; taceleresen, 30—35; bitter-principle, 0·5; impurities, 15.

C. F. B.

Genuine Tacamahac of Commerce. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1904, **242**, 395—400).—The sample examined was of unknown origin, but may be taken as typical of those Tacamahaca resins which are entirely amorphous (compare preceding abstract); it melted at 85—87° and had acid number 8·8, saponification number 36·4. From a solution of the resin in ether, 1 per cent aqueous ammonium carbonate extracted amorphous *tacamahic acid*, $C_{43}H_{72}O_2$, melting at 95°. One per cent. aqueous sodium carbonate then extracted amorphous *tacamaholic acid*, $C_{15}H_{25}O_2$; this melts at 104—106° and is monobasic. The remaining solution, when distilled with steam, yielded an *essential oil* boiling for the most part at 170—175°, whilst amorphous takoresen remained behind; this was separated into α- and β-*takoreses*, respectively insoluble and soluble in dilute alcohol of sp. gr. 0·892; the first, $C_{21}H_{33}O$, melts at 93—95°, the second, $C_{15}H_{25}O$, at 82°. A *bitter-principle* was also present, and when the resin is dissolved in ether, *tacamahaca gum*, $C_6H_{10}O_5$, remained undissolved. Evidently the substance does not belong to the group of elemi resins.

In 100 parts of the resin are contained: gum, 3; tacamahic acid, 0·5; tacamaholic acid, 0·5; essential oil, 3; α-takoresen, 50; β-takoresen, 30; bitter-principle, 0·5; impurities, 10. C. F. B.

Resins of the Elemi Group. ALEXANDER TSCHIRCH and OTTO SAAL (*Arch. Pharm.*, 1904, **242**, 366—373).—A summary of the results obtained hitherto (Abstr., 1902, i, 812; 1903, i, 430; this vol., i, 332, 758). The resin acids in general may be referred to two groups: eleminic acids, with the formula $C_{39}H_{56}O_4$, and elemic acids, $C_{37}H_{56}O_4$. The *iso*eleminic acids are extracted by 1 per cent. aqueous ammonium carbonate, are amorphous, and melt at 75°; the eleminic acids are extracted by 1 per cent. aqueous sodium carbonate, are crystalline, and melt at 215°. The *iso*elemic acids are extracted by 1 per cent. aqueous ammonium or sodium carbonate, are amorphous, and melt at 120°; the elemic acids are extracted by 1 per cent. aqueous sodium carbonate or potassium hydroxide and are crystalline, melting at 215°, or amorphous, melting at 120°.

Generally the resins melt between 70° and 77°, and vary not inconsiderably in composition, approximating, however, to that required by $C_{15}H_{24}O$, the formula of an oxysesquiterpene. C. F. B.

Rutin from Rue (Ruta Graveolens). N. WALIASCHKO (*Arch. Pharm.*, 1904, 242, 225—254).—Rutin was extracted from the dry herb by repeated boiling with water; it formed a yellow, crystalline powder melting at 188—190° and dissolved in 200 parts of cold, 7800 of boiling, water. It has the composition $C_{27}H_{30}O_{16},3H_2O$, but easily loses $1H_2O$ in the air. When it is boiled with 10 per cent. nitric acid, it yields oxalic acid and a nitro-compound resembling picric acid. Boiling with 1 per cent. sulphuric acid hydrolyses it to quercetin, rhamnose, and dextrose.

Rutinquercetin is identical with the quercetin formed from quercitrin, and both substances form identical acetyl, ethyl, and acetylethyl derivatives. Rutinquercetin is a yellow, crystalline powder with the composition $C_{15}H_{10}O_7,2H_2O$; it melts and decomposes at 310°. *Penta-acetylquercetin*, $C_{15}H_5O_7Ac_5$, melts at 191—192°. *Tetraethylquercetin*, $C_{15}H_6O_7Et_4$, melts at 121° and forms a yellow *monopotassium* derivative; *acetyltetraethylquercetin*, $C_{15}H_5O_7Et_4Ac$, melts at 152—153°. The last substance yields a mixture of di- and tri-ethylquercetins when it is hydrolysed; when this mixture is boiled with ethyl iodide and alcoholic potassium hydroxide, *triethylquercetin*, $C_{15}H_7O_7Et_3$, is formed; this is pale yellow, melts at 123—124°, and forms a yellow *dipotassium* derivative. In the ethylation of quercetin with ethyl iodide and alcoholic potassium hydroxide there are formed, in addition to the tetraethyl derivative, yellow *prisms* melting at 116°, possibly $C_{15}H_7O_7Et_3,C_{15}H_6O_7Et_4$, and yellowish-white spherical aggregates melting at 110°.

When quercetin in warm methyl-alcoholic solution is mixed with methyl sulphate and potassium hydroxide is added gradually, yellow *trimethylquercetin*, $C_{15}H_7O_7Me_3$, melting at 154°, is formed together with small quantities of two other yellow substances melting at 240° and 175° respectively. The trimethyl derivative forms a yellow potassium derivative, little soluble in alcohol and decomposed by water; if this is mixed with methyl sulphate in a mortar, *pentamethylquercetin*, $C_{15}H_5O_7Me_5,H_2O$, is formed; this melts at 148° and forms no potassium derivative.

The quercetin from rutin also agrees with that from quercitrin in yielding phloroglucinol and protocatechuic acid when fused with potassium hydroxide.

From the product of the hydrolysis of rutin with 1 per cent. sulphuric acid, after separation of the quercetin, rhamnose was isolated in the pure state and identified carefully. There remained an uncrystallisable syrup, which was identified with dextrose. The amount of quercetin formed in the hydrolysis of rutin, and of methylfurfural phloroglucide obtained (from the rhamnose) when rutin is distilled with 12 per cent. hydrochloric acid and phloroglucinol added to the distillate, and the rotation of the liquid left after hydrolysis, all harmonise with the equation $C_{27}H_{30}O_{16} + 3H_2O = C_{15}H_{10}O_7$ (quercetin) +

$C_6H_{14}O_6$ (rhamnose) + $C_6H_{12}O_6$ (glucose) as expressing the hydrolysis of rutin.

Rutin can be acetylated with acetic anhydride and methylated with methyl sulphate, but in neither case would the derivative crystallise.

The seeds of *Ruta graveolens* contain, in addition to rutin, an alkaloid (choline ?), the *aurichloride* of which contains Au 45·4, Cl 31·6 per cent.; an acid (*rutic acid*), which was only obtained as a resinous solid; and a *resin*, which was obtained crystalline from alcohol.

Incidentally, it was found that Seliwanoff's reaction for lævulose (Abstr., 1887, 459), or more generally for all ketoses (Neuberg, *Zeit. physiol. Chem.*, 1900, 31, 566), is given by the syrups that are obtained in the hydrolysis of quercitrin, rutin, and robinin, although these only contain respectively rhamnose, rhamnose and glucose, and rhamnose and galactose in appreciable quantity. C. F. B.

Saponin Substances of Dioscorea Tokoro Makino. J. Honda (*Chem. Centr.*, 1904, ii, 118—119; from *Arch. exp. Path. Pharm.*, 1904, 51, 211—226).—The roots of *Dioscorea Tokoro Makino*, or the Japanese Oni-Tokoro or Tokoro, contain two saponin substances, dioscin and dioscorea sapotoxin. *Dioscin*, $C_{24}H_{38}O_9,3H_2O$, extracted from the roots by means of 96 per cent. alcohol, crystallises from absolute alcohol in white needles which have a silky lustre and melt at 247—250°. Dioscin is readily soluble in alcohol, methyl alcohol, or glacial acetic acid, sparingly so in hot water, chloroform, amyl alcohol, or acetone, very sparingly so in cold water, and insoluble in ether or light petroleum. The alcoholic solution is dextrorotatory, and the aqueous solution froths readily. It forms a yellow solution in concentrated sulphuric acid, which becomes successively reddish-yellow, dark red, and violet. Potassium dichromate and potassium permanganate give green and violet colorations respectively with solutions in concentrated sulphuric acid. Dioscin dissolves in Frohde's reagent, forming a yellow solution which turns violet. Warm concentrated nitric acid gives a yellow solution, and on boiling with concentrated hydrochloric acid the liquid froths and white flakes are formed. When boiled with dilute acids, dioscin yields a dextrorotatory sugar together with a compound which crystallises from alcohol in leaflets, and is readily soluble in ether, alcohol, methyl alcohol, or light petroleum. The *acetyl* derivative is an amorphous substance and is readily soluble in ether, chloroform, benzene, alcohol, or glacial acetic acid. *Sapotoxin*, $C_{23}H_{38}O_{10}$, isolated from the roots by means of lead acetate and magnesia, is a white, deliquescent, amorphous powder, melts at 172°, and is soluble in alcohol or methyl alcohol, but only very sparingly so in ether, chloroform, amyl alcohol, acetone, light petroleum, or carbon disulphide. It is readily soluble in water; a solution containing 1 part in 200,000 of water froths. The aqueous solution is lævorotatory. With concentrated sulphuric acid, potassium permanganate, potassium dichromate, and nitric acid it gives the same reactions as dioscin, and with hot concentrated hydrochloric acid it develops a ruby-red coloration. By the action of dilute acids, with the exception of nitric acid, acetic acid, and phosphoric acid, it forms flocculent precipitates on boiling. When boiled with acids, a compound which has reducing

properties is formed together with a substance which is readily soluble in alcohol or ether, but insoluble in water. The *benzoyl ester* is a colourless, amorphous substance and is readily soluble in ether, chloroform, or benzene.

Dioscin and sapotoxin have a poisonous action on fish, that of the former being the stronger. Solutions of sapotoxin also destroy tænia. The hæmolytic action of dioscin is greater than that of any other saponin; sapotoxin has only a feeble action. Amœbæ, when immersed in a solution of sapotoxin, are quickly reduced to a mass of detritus. Dioscin is tasteless, and neither induces sneezing nor a burning sensation in the nose, but it has an irritating action on the conjunctiva. Solutions of sapotoxin which contain only 1 part in 10,000 of water have an intensely bitter taste. Dioscin, when administered to dogs *per os*, acts as a slight emetic. Subcutaneous injection of either compound causes local irritation in the case of frogs, and feeble paralysis of a central nature with complete immobility of the muscles; with warm-blooded animals only local irritation is caused. E. W. W.

Substantive Dyes containing Sulphur. FRITZ POLLAK (*Zeit. Farb. Text. Ind.*, 1904, 3, 233—237, 253—258).—A *résumé* of the subject, with an attempt at classification. W. A. D.

Action of Hydroxylamine on Ethyl Dimethylpyronedicarboxylate. F. CARLO PALAZZO (*Gazzetta*, 1904, 34, i, 458—482. Compare Abstr., 1902, i, 816).—The action of hydroxylamine on ethyl dimethylpyronedicarboxylate yields a *compound*, $C_7H_9O_4N$, which separates from water in shining crystals containing H_2O and melting at 166°. It acts towards potassium hydroxide as a monobasic acid, and forms a *silver* salt, $C_7H_8O_4NAg$, and an *ethyl* ester, $C_7H_8O_3N{\cdot}OEt$, which crystallises from water in silky needles, melting at 80°, and is readily hydrolysed. On heating the compound or its salts with dilute sulphuric acid, decomposition takes place according to the equation:

$$C_7H_9O_4N + 4H_2O = NH_2{\cdot}OH + 2CH_3{\cdot}CO_2H + CO_2 + EtOH.$$

Oxidation with permanganate yields nitrous, nitric, acetic, and oxalic acids.

The compound probably has the constitution $\mathrm{OH{\cdot}N{:}\overset{O\cdot CMe}{C{\cdot}C}{\cdot}CO_2Et}$, corresponding with the formula given by Conrad and Guthzeit for ethyl dimethylpyronedicarboxylate, namely,

$$\mathrm{COMe{\cdot}C(CO_2Et){:}\overset{O\cdot CMe}{C{\cdot}C}{\cdot}CO_2Et.}$$

T. H. P.

Researches in the Pyran [1 : 4-Pent-furfuran] Series. EDMOND E. BLAISE and H. GAULT (*Compt. rend.*, 1904, 139, 137—139).—Ethyl oxalacetate condenses with formaldehyde in the presence of piperidine to form the *compound* $CH_2[CH(CO_2Et){\cdot}CO{\cdot}CO_2Et]_2$, which crystallises from ether, melts at 80—81°, gives a red coloration with ferric chloride, combines readily with 1 mol. of water or hydrogen sulphide, gives crystalline derivatives with phenylhydrazine or hydrazine, and loses

carbon dioxide on hydrolysis with hydrochloric acid, forming *diketo-pimelic acid* [$\alpha\epsilon$-diketopentane-$\alpha\epsilon$-dicarboxylic acid],

$$CO_2H\cdot CO\cdot[CH_2]_3\cdot CO\cdot CO_2H,$$

in the form of colourless crystals melting at 127°, and converted into pimelic acid by hydrogenation and reduction, and into the dinitrile of glutaric acid by decomposing the dioxime with boiling water. Diketo-pimelic acid forms crystalline metallic salts, hydrazone, phenylhydrazone, semicarbazone, oxime, and condensation products with aniline or potassium hydrogen sulphite and yields *pyran-2 : 6-dicarboxylic acid*, $CH_2{<}{CH{:}C(CO_2H) \atop CH{:}C(CO_2H)}{>}O$; on dehydration, the new acid crystallises in colourless needles, decomposes at 250°, and yields crystalline salts and esters. M. A. W.

Synthesis of Galangin. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and JOSEF TAMBOR (*Ber.*, 1904, **37**, 2803—2806).—The synthesis of 5 : 7-dihydroxyflavonol is described and the identity of this substance with the naturally-occurring galangin established.

When 2′-hydroxy-4′ : 6′-dimethoxychalkone (Kostanecki and Tambor, Abstr., 1899, i, 892) in alcoholic solution is heated with dilute hydrochloric acid, it undergoes transformation into 5 : 7-*dimethoxyflavanone*, $\begin{matrix} C(OMe){:}CH\cdot C{-}O\cdot CHPh \\ CH{:}C(OMe)\cdot C\cdot CO\;CH_2 \end{matrix}$, which separates from alcohol in colourless, prismatic needles and melts at 146—147°; it forms yellow solutions with alcoholic sodium hydroxide and with concentrated sulphuric acid. Its 3-iso*nitroso*-derivative, prepared by the action of amyl nitrite and hydrochloric acid, crystallises from benzene in yellow needles and melts and decomposes at 175—177°.

5 : 7-*Dimethoxyflavonol* crystallises from alcohol in yellow prisms and melts at 177—178°; it forms an intensely-yellow sodium salt; its solution in concentrated sulphuric acid is greenish-yellow and exhibits green fluorescence. Its *acetyl* derivative separates from dilute alcohol in white needles and melts at 192—193°.

5 : 7-*Dihydroxyflavonol* (galangin), $\begin{matrix} C(OH){:}CH\cdot C{-}O{-}CPh \\ CH{:}C(OH)\cdot C\cdot CO\cdot C\cdot OH \end{matrix}$, prepared by boiling 5 : 7-dimethoxyflavonol with concentrated hydriodic acid, contains $1H_2O$; it crystallises from dilute alcohol in yellowish-white needles and melts at 217—218°. For the natural product, Jahns gives 214—215° and Testoni 219—221°. The colour reaction of the synthesised product, when dissolved in concentrated sulphuric acid, was identical with that of the natural product. The *acetyl* derivative, prepared both from the natural and from the synthesised product, crystallises from alcohol in silky needles and melts at 140—142°.

A. McK.

An Isomeride of Galangin. F. DOBRZYŃSKI and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, **37**, 2806—2809).—7 : 8-Dimethoxyflavanone is best prepared by the action of dilute sulphuric acid on an alcoholic solution of 2′-hydroxy-3′ : 4′-dimethoxychalkone, obtained by the action of benzaldehyde on gallacetophenonedimethylether.

3-iso*Nitroso*-7 : 8-*dimethoxyflavanone*, prepared by the action of amyl nitrite and fuming hydrochloric acid on 7 : 8-dimethoxyflavanone, crystallises from benzene in white needles and melts and decomposes at 166°. Its solution in dilute aqueous sodium hydroxide is yellow. When dissolved in acetic acid and then boiled with dilute sulphuric acid, hydroxylamine and 7 : 8-*dimethoxyflavonol* are formed; the latter separates from alcohol in yellow needles and melts at 203°; its solution in concentrated sulphuric acid is greenish-yellow; its *acetyl* derivative crystallises from alcohol in white plates and melts at 185°. When boiled with hydriodic acid, it is converted into 7 : 8-*dihydroxyflavonol*, which separates from dilute alcohol in pale yellow needles and melts at 249°. Its solutions in alkalis are reddish-yellow; its solution in concentrated sulphuric acid is yellow. Its *acetyl* derivative crystallises from alcohol in white needles and melts at 210°.

A. McK.

Synthesis of Flavonol. STANISLAUS VON KOSTANECKI and W. SZABRAŃSKI (*Ber.*, 1904, 37, 2819—2820).—When flavanone,

$$C_6H_4<\begin{matrix}O-CHPh\\CO\cdot CH_2\end{matrix}$$

(compare this vol., i, 684), is acted on by amyl nitrite and hydrochloric acid, it is converted into 3-iso*nitrosoflavanone*, $C_6H_4<\begin{matrix}O-CHPh\\CO\cdot C{:}NOH\end{matrix}$, which melts and decomposes at 158—159°. When boiled with dilute mineral acids, hydroxylamine is eliminated, whilst *flavonol*,

$$C_6H_4<\begin{matrix}O-CPh\\CO\cdot C\cdot OH\end{matrix},$$

is produced; it crystallises from alcohol in yellow needles and melts at 169—170°. It forms a yellow solution when warmed with aqueous sodium hydroxide; on cooling, the sparingly soluble *sodium* salt separates in yellow needles. The solution of flavonol in concentrated sulphuric acid exhibits an intense violet fluorescence. Its *acetyl* derivative separates from dilute alcohol in glistening needles and melts at 110—111°.

A. McK.

Condensation of Hydroxyquinol with Aldehydes. CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1904, 37, 2728—2737. Compare this vol., i, 443).—2 : 3 : 7-Trihydroxy-9-methylfluorone may readily be obtained in the form of its sulphate by mixing an alcoholic solution of hydroxyquinol and paracetaldehyde with 15 per cent. sulphuric acid. It forms orange-red needles, and on solution in alcohol containing a few drops of sulphuric acid and precipitation with water yields the free base in the form of dark red needles with a metallic lustre. The *acetyl* derivative forms pale yellow needles, melts at 225—228°, and its solutions do not exhibit fluorescence.

2 : 3 : 7-*Trihydroxy*-9-m-p-*dihydroxyphenylfluorone*,

$$\begin{matrix}OH\cdot C{:}CH\cdot C{:}C[C_6H_3(OH)_2]\\O{:}C\cdot CH{:}C\cdot O\text{———————}\end{matrix}>C_6H_2(OH)_2,$$

is obtained as the *sulphate*, $(C_{19}H_{12}O_7)_2,H_2SO_4,H_2O$, when an aqueous alcoholic solution of hydroxyquinol and procatechuic aldehyde is left in

contact with concentrated sulphuric acid for some 5 weeks. When boiled with water, the sulphate is decomposed and yields a precipitate of the *base* in the form of small, orange-red needles with a metallic lustre. It melts above 300° and is sparingly soluble in the usual solvents. Its alcoholic solution has a strong, yellowish-green fluorescence, and it dissolves in alkalis, yielding red solutions with a pale red fluorescence. The *penta-acetyl* derivative melts at 227—231°.

Hydroxyquinol and *p*-hydroxybenzaldehyde in presence of sulphuric acid yield 2 : 3 : 7-*trihydroxy*-9-p-*hydroxyphenylfluorone sulphate* in the form of an intense yellow, voluminous precipitate. The *base* forms orange-red needles with a metallic lustre, and the *tetra-acetyl* derivative melts at 242—243°. 2 : 3 : 7-*Trihydroxy*-9-o-*hydroxyphenylfluorone*, obtained from salicylaldehyde and hydroxyquinol, yields a *sulphate* in the form of compact, glistening, red needles; the *base* crystallises in brownish-red needles, is extremely readily soluble in alcohol, and yields an *acetyl* derivative melting at 223—224°. 2 : 3-*Dihydroxyxanthen*,

$$C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{O}>C_6H_2(OH)_2,$$

may be obtained from the mother liquor from which the sulphate separates. It crystallises from hot water in rose-coloured plates melting at 173—175° and readily soluble in the common organic solvents. It also dissolves in alkali or concentrated sulphuric acid, but none of the solutions fluoresces. The *diacetyl* derivative crystallises in long, glistening needles, sinters at 100°, melts at 110°, and on oxidation with chromic acid yields *diacetoxyxanthone*,

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{O}>C_6H_2(OAc)_2,$$

which crystallises in glistening needles melting at 186°. When treated with cold concentrated sulphuric acid, or when boiled with dilute alkali, it yields the corresponding *dihydroxyxanthone*, which crystallises from alcohol in long, yellow needles resembling anthraquinone. It melts at 294°, is sparingly soluble in chloroform, and solutions in organic solvents are practically colourless. Its solution in concentrated sulphuric acid fluoresces, and its solutions in alkalis have an intense yellow colour. It has practically no dyeing properties, and thus differs from the isomeric 3 : 4-dihydroxyxanthone (Graebe and Eichengrün, Abstr., 1891, 706). Salicylaldehyde and resorcinol condense in aqueous alcoholic solution, and in the presence of sulphuric acid at 100°, yielding colourless needles which appear to be a mixture of two compounds, since, when acetylated, two *acetyl* derivatives are obtained. The one of these, $C_{13}H_7O_3Ac_2$, is insoluble in alcohol, crystallises in colourless, glistening plates, does not melt below 300°, and is sparingly soluble in the usual solvents.

The second compound, which is isomeric, melts at 270—275° and dissolves readily in the usual solvents. J. J. S.

Condensation of Cotarnine and of Hydrastinine with Ketones. Carl Liebermann and A. Glawe (*Ber.*, 1904, 37, 2738—2744. Compare this vol., i, 263).—Cotarnine and hydrastinine yield condensation products with most compounds containing a methylene group between two carbonyl groups; they also react with

coumarone, resorcinol, quinol, and other compounds, but not with meconine. Some of the condensation products are relatively stable; others, for example, those with ethyl malonate derivatives, are readily hydrolysed to their components. In many of the condensations, piperidine gives better yields than sodium carbonate solution. Most of the condensation products appear to have a hydrogen atom attached to nitrogen, and are to be represented by the formula

$CH_2{:}O_2{:}C_6H(OMe)(CH{:}CH{\cdot}COX){\cdot}CH_2{\cdot}CH_2{\cdot}NHMe$.

Ethyl anhydrocotarninephenylacetate,

$CH_2{:}O_2{:}C_6H(OMe)(CH{:}CPh{\cdot}CO_2Et){\cdot}CH_2{\cdot}CH_2{\cdot}NHMe$,

crystallises from alcohol in colourless prisms melting at 91—92°. The *platinichloride* is precipitated as a yellow, flocculent mass and the *nitrate* as small and sparingly soluble needles.

Ethyl anhydrohydrastininephenylacetate melts at 85—86° and the nitrate is readily soluble.

Ethyl anhydrocotarninemalonate,

$CH_2{:}O_2{:}C_6H(OMe)(CH_2{\cdot}CH_2{\cdot}NHMe){\cdot}CH_2{:}C(CO_2Et)_2$,

forms a colourless, crystalline powder melting at 73° and readily soluble in the usual organic solvents. On treatment with chloroplatinic acid, it is decomposed and yields cotarnine platinichloride. The *methiodide* crystallises in colourless needles melting at 201°.

Ethyl anhydrohydrastininemalonate melts at 55—57°, is readily soluble in alcohol, and is very unstable.

Anhydrocotarninecoumaron, $C_{12}H_{14}O_3N{\cdot}C_8H_5O$, is precipitated on the addition of light petroleum to its ethereal solution as a yellow, amorphous mass melting at 66—71°; the *platinichloride* is also amorphous. The corresponding *hydrastinine* derivative melts at 68—70° and dissolves in concentrated sulphuric acid to a violet-coloured solution.

Anhydrocotarnineresorcinol, obtained without the aid of a condensing agent, melts and decomposes at 220°, is only sparingly soluble in the usual solvents, but dissolves in dilute acids. The *hydrochloride* is somewhat sparingly soluble in hydrochloric acid and melts at 242°.

J. J. S.

Condensations with Cotarnine. F. Kropf (*Ber.*, 1904, 37, 2744—2750. Compare this vol., i, 263 and preceding abstract).—*Anhydrocotarnine acetylacetone*, $C_{17}H_{21}O_5N$, crystallises in colourless prisms melting at 98—99°; the *hydrochloride* crystallises in glistening, hygroscopic needles and the *platinichloride* in yellow needles. *Anhydrocotarnineacetonylacetone*, $C_{18}H_{23}O_5N$, melts at 147—149° and is readily soluble in alcohol or ether. *Ethyl anhydrocotarnineacetoacetate*, $C_{18}H_{23}O_6N$, crystallises in colourless needles melting at 59—60°. *Ethyl anhydrocotarninebenzoylacetate*, $C_{23}H_{24}O_6N$, melts at 100—102° and yields a *platinichloride* melting at 116—117°.

Ethyl anhydrocotarninecyanoacetate, $C_{17}H_{20}O_5N_2$, melts and decomposes at 95—96° and is extremely unstable. *Ethyl anhydrocotarnine-ethylacetoacetate*, $C_{20}H_{27}O_6N$, is an oil and yields a *hydrochloride* which crystallises in colourless needles. The corresponding *derivative* of ethyl benzylacetoacetate is also an oil.

Methyl iodide reacts in the cold with a methyl-alcoholic solution of

anhydrocotarnineacetophenone (this vol., i, 263), yielding a mixture of the corresponding hydriodide, which is readily soluble in water, and the *methiodide*, which crystallises from alcohol in colourless needles melting at 225—226°. If the mixture is not kept cool, the product is *anhydromethylcotarnineacetophenone hydriodide*. This crystallises in long, colourless needles, melts at 171°, and is readily soluble in alcohol or water. The addition of alkali to the aqueous solution yields the *base*, $C_{21}H_{23}O_4N$, which melts at 78°. Anhydrocotarnineacetophenone, on treatment with acetic anhydride, yields an *acetyl* derivative, which crystallises in colourless needles melting at 139—140°; the *benzoyl* derivative melts at 107—108°. The *benzoyl* derivative of anhydrocotarnineacetone, obtained by direct benzoylation of anhydrocotarnineacetone or by the condensation of benzoylcotarnine (Roser, Abstr., 1890, 528), melts at 124°. These reactions indicate the presence of an NH group in anhydrocotarnine-acetone and -acetophenone.

J. J. S.

Constitution of Thebenine. ROBERT PSCHORR and CORNELIUS MASSACIU (*Ber.*, 1904, 37, 2780—2792. Compare Freund, Abstr., 1899, i, 307).—When thebaine is heated with hydrochloric acid, one of the methyl groups is hydrolysed and at the same time the tertiary is converted into a secondary base. Contrary to the observations of Freund, the methyl ether, methebenine, of thebenine is soluble in alkalis and has a phenolic character, although in dilute solutions it requires six mols. of alkali for dissolution; the third oxygen atom, not accounted for by the two methyl groups, is therefore phenolic and does not form part of a furane ring. Hence thebenine may be formulated as $OH\cdot C_{16}H_{10}(OMe)_2\cdot NHMe$. The hydroxyl group cannot be methylated until the secondary nitrogen has been converted into a quaternary compound, but the product, $C_{16}H_{10}(OMe)_3NMe_3I$, when heated with alkali hydroxides, loses trimethylamine and gives a trimethoxyphenanthrene derivative, $C_{14}H_6(OMe)_3\cdot CH{:}CH_2$, which was oxidised to trimethoxyphenanthrenecarboxylic acid,

$$C_{14}H_6(OMe)_3\cdot CO_2H,$$

proving that all three oxygen atoms of methebenine are directly linked to the phenanthrene nucleus. The formula

$$C_{14}H_6(OMe_2)(OH)\cdot CHMe\cdot NHMe$$

is suggested for thebenine.

Diacetylmethebenine, $C_{23}H_{15}O_5N$, prepared by the action of acetic anhydride on a cold alkaline solution of methebenine, was found to be identical with the compound which Freund obtained by boiling with sodium acetate and acetic anhydride, a process which Freund assumed to be accompanied by a splitting of the furane ring, which can hardly be supposed to occur under the milder conditions now employed. Under similar conditions, benzoyl chloride gives a *dibenzoyl* derivative, $C_{33}H_{29}O_5N$, which crystallises from alcohol in needles and melts at 159° (corr.).

Dimethebeninmethine methiodide, $C_{16}H_{10}(OMe)_3\cdot NMe_3I$, prepared by the action of potassium iodide on the methylsulphate, crystallises from alcohol in bundles of needles and melts at 247° (corr.). The

methylsulphate, $C_{16}H_{10}(OMe)_3\cdot NMe_3\cdot SO_4Me$, crystallises in colourless needles, sinters at 268°, and melts at 270° (corr. 277°).

Trimethoxyvinylphenanthrene, $C_{16}H_9(OMe)_3$, prepared by heating either of the preceding compounds with potassium hydroxide, crystallises from alcohol in well-formed, pale yellow tablets and melts at 122·5° (corr.). The *picrate* forms red, quadrilateral tablets and melts at 110°.

Trimethoxyphenanthrenecarboxylic acid, $C_{18}H_{16}O_5$, crystallises from acetic acid in small, yellow needles and melts at 219—221° (corr.).

Boiling in acetic acid solution, or with a little hydrochloric acid in alcoholic solution, converts the vinyl derivative into Freund's methebenol, a compound which contains no hydroxyl group and is formulated as $C_{14}H_6(OMe)_2{<}{\substack{-O-\\ CH_2}}{>}CH_2$, and bromination of the vinyl derivative yields a bromomethebenol,

$$C_{14}H_{16}(OMe)_2{<}{\substack{-O-\\ CHBr}}{>}CH_2,$$

which crystallises from chloroform in needles and melts at 148—149° to a liquid which decomposes at 205—207°. T. M. L.

isoCreatinine and its Identity with Creatinine. E. Poulsson (*Chem. Centr.*, 1904, ii, 30—31; from *Arch. exp. Path. Pharm.*, 1904, 51, 227—238).—Thesen's *iso*creatinine (Abstr., 1898, i, 387) is impure creatinine which contains a yellow dye. The latter may be removed by heating with animal charcoal or by purification by means of the sulphate. The substance prepared according to Thesen's directions gives all the reactions of ordinary creatinine and does not exhibit any peculiar or characteristic behaviour. The flesh of cod contains 0·2, of halibut 0·17, and of mackerel 0·22 per cent. of creatinine, whilst 0·055 per cent. is present in lean beef.

Creatinine tartrate, $(C_4H_7ON_3)_2,C_4H_6O_6$, crystallises in needles, decomposes at 207—209°, and is readily soluble in water, but only sparingly so in alcohol. *Creatinine oxalate*, $(C_4H_7ON_3)_2,C_2H_2O_4$, crystallises in prisms and is soluble in water, but only very sparingly so in alcohol. E. W. W.

isoCreatinine. G. Korndörfer (*Arch. Pharm.*, 1904, 242, 373—379).—The author has arrived independently at the same conclusion as Poulsson (preceding abstract), namely, that the *iso*creatinine of Thesen (Abstr., 1898, i, 387) is identical with the creatinine of urine, &c. "*iso*Creatinine" was prepared from the flesh of the cod, and obtained colourless by passage through the hydrochloride or platinichloride; it was found to be identical with creatinine from urine in a number of physical properties and chemical reactions. C. F. B.

Damascenine. Oskar Keller (*Arch. Pharm.*, 1904, 242, 299—327. Compare Pommerehne, Abstr., 1899, i, 964; 1900, i, 684; 1901, i, 289; this vol., i, 685).—When the hydrochloride of damascenine, $C_9H_{11}O_3N_3$, is treated with bromine in alcoholic solution and

the solution eventually diluted with ether, crystals of a salt, $C_9H_{11}O_3NBr_2,HBr$, separate; these melt at 198—201.°

Damascenine is converted into a *monacetyl* derivative, $C_9H_{10}O_3NAc$, melting at 203—204°, when its hydrochloride is boiled with acetic anhydride.

Damascenine is transformed, when it is boiled with alcoholic potash or other alkalis, into a monobasic acid, damasceninic acid, isomeric with damascenine (molecular weight determined), and still containing a methoxyl group; some salts of this substance, which has the character of an amino-acid, have been described already. The *hydrobromide*, $C_9H_{11}O_3N,HBr,H_2O$, melting at 204—206°, the *sulphate*, $C_9H_{11}O_3N,H_2SO_4,H_2O$, melting at 209—210°, and the amorphous *silver* and green, crystalline *copper* salt, $(C_9H_{10}O_3N)_2Cu,\frac{1}{2}H_2O$, melting at 215—217°, have been analysed; other copper salts seem capable of existence. A *methyl* ester appears to exist, of which the *hydrochoride*, $C_9H_{10}O_3NMe,HCl,H_2O$, melts at 199—200° when dried.

Bromine in alcoholic solution converts damasceninic acid into a substance, $C_9H_{11}O_3NBr_2$, which melts at 206—208°. Acetic anhydride converts it into the same acetyl compound as was obtained from damascenine itself; this acetyldamascenine does not form an additive compound with methyl iodide, and therefore probably contains the acetyl group attached to the nitrogen atom.

Methyl iodide converts damasceninic acid into the same hydriodide as is obtained in similar circumstances from damascenine itself; the free *base*, $C_9H_{10}O_3NMe$, melts at 118—119°. The further action of methyl iodide leads to the formation of a quaternary *iodide*, $C_9H_{10}O_3NMe,MeI,H_2O$, melting at 175—176° (at 164—166° when dried); the corresponding *hydrochloride* (not analysed) melts at 185—186°; the hydroxide appears to undergo no decomposition when its aqueous solution is distilled.

Nitrous acid converts both damascenine and damasceninic acid into a *nitroso*-derivative, which melts at 151—152°.

When damasceninic acid is boiled for a comparatively short time with hydriodic acid (b. p. 127°), 1 mol. proportion of methyl iodide is evolved; this is followed by a second if the heating is prolonged. When damascenine is heated with hydriodic acid for several hours at 150—160°, *o*-aminophenol is obtained together with a little of a *hydriodide*; the latter contains I 55·6 per cent. and melts at 213—214°; after it has been crystallised from water, a *compound* free from iodine and melting at 240—260° is obtained.

Evidently damasceninic acid may be formulated as

$$NHMe\cdot C_6H_3(OMe)\cdot CO_2H\ [NHMe : OMe : CO_2H = 1 : 2 : ?].$$

C. F. B.

Conversion of Ephedrine into ψ-Ephedrine. F. Flaecher (*Arch. Pharm.*, 1904, **242**, 380—383).—By heating ephedrine with 5 per cent. hydrochloric acid at 170—180° for 5 hours it was converted into the "*iso*ephedrine" of Nagai (*Chem. Zeit.*, 1890, 441); this, however, is found to be nothing else but the ψ-ephedrine of Ladenburg and Oelschlägel (Abstr., 1889, 1020). C. F. B.

Poisonous Constituent of the Alpine Salamander, Salamandra Atra. FRITZ NETOLITZKY (*Chem. Centr.*, 1904, ii, 130—131; from *Arch. exp. Path. Pharm.*, 1904, 51, 118—129).—*Samandatrine,* prepared from the alcoholic extract of the macerated flesh and slimy secretions of *Salamandra atra,* forms a clear yellow syrup which is very readily soluble in hot amyl alcohol, readily so in ether or chloroform, and very sparingly so in cold water or alcohol. It is distinguished from the alkaloids samandarine and samandaridine, from *S. maculosa,* by its solubility in ether. The solutions of samandatrine have an alkaline reaction and are precipitated by alkaloidal reagents. When boiled for a few minutes with concentrated hydrochloric acid, a faint violet coloration is formed which becomes bluish-red in 24 hours, and by repeatedly evaporating with the acid a blue, amorphous residue is left. Concentrated sulphuric acid dissolves samandatrine, forming a pale yellow solution which, after several days, becomes pale violet. The *sulphate,* $(C_{21}H_{37}O_3N_2)_2H_2SO_4$?, crystallises in white needles, has a very bitter taste, and is sparingly soluble in water. About 1 milligram of the sulphate can be prepared from one salamander. The physiological action of the alkaloid resembles that of the alkaloids of *S. maculosa* (compare Faust, Abstr., 1899, i, 380). The results of experiments on cold-blooded animals show that the alkaloid probably attacks the central nerve system.

E. W. W.

Oxidation of Pyrrole to Maleimide. GIUSEPPE PLANCHER and F. CATTADORI (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 489—492).—*Maleimide,* $NH<\begin{matrix}CO\cdot CH \\ CO\cdot CH\end{matrix}$ (with the two CH joined by a double bond), prepared by the oxidation of pyrrole, separates from ethyl acetate in faintly yellow crystals melting at 93°; it readily sublimes in shining, slender plates and has a pungent odour, while its vapours attack the mucous membrane of the nose and eyes. With ammoniacal silver nitrate solution, it yields a crystalline precipitate, which separates from water in colourless plates. When treated with bromine water in the light, it yields the dibromide melting at about 226°.

T. H. P.

Trichloropyrrole. V. GIROLAMO MAZZARA and A. BORGO (*Gazzetta*, 1904, 34, i, 414—420).—The trichloropyrrole (Abstr., 1904, i, 614), formed by the action of sulphuryl chloride ($3\frac{1}{2}$ mols.) on pyrrole (1 mol.), is obtained in almost theoretical yield when the products of the reaction are distilled in a current of steam under 100 mm. pressure, the receiver being covered with a black cloth. Trichloropyrrole undergoes change extremely readily when subjected to the action of light or air. When gradually added to concentrated nitric acid of sp. gr. 1·48, it yields the chloromaleimide obtained by Ciamician and Silber (Abstr., 1884, 293) by the action of chlorine on succinimide, together with small quantities of dichloromaleimide apparently formed from traces of tetrachloropyrrole admixed with the trichloro-compound.

As the reaction between sulphuryl chloride and pyrrole only pro-

ceeds readily in the absence of moisture, freshly purified materials should be employed, as well as absolutely anhydrous alcohol.

T. H. P.

Bromotrichloromethylpyrrole and Chlorobromomaleic Methylimide. VI. Girolamo Mazzara (*Gazzetta*, 1904, 34, i, 482—491. Compare preceding abstract).—2 : 3 : 5-*Trichloro-4-bromo-1-methylpyrrole*, $C_5H_3NCl_3Br$, prepared by passing bromine vapour slowly into 2 : 3 : 5-trichloro-1-methylpyrrole suspended in water, or by the action of bromine on a solution of 2 : 3 : 5-trichloro-1-methylpyrrole in glacial acetic acid, crystallises from alcohol in slender, white, silky needles, melting at 120°. It volatilises with difficulty in a current of steam, sublimes with slight decomposition at 100°, and is soluble in sulphuric acid developing a red coloration ; in benzene, it exhibits normal cryoscopic behaviour.

The action of cold fuming nitric acid on this compound yields *chlorobromomaleic methylimide*, $NMe<\begin{matrix}CO\cdot CBr\\ \quad\ \ \|\\ CO\cdot CCl\end{matrix}$, which sublimes in shining, pale yellow laminæ, composed of long, flattened needles melting at 103°.

The oxidation of 2 : 3 : 4 : 5-tetrachloro-1-methylpyrrole with either bromine or nitric acid yields dichloromaleic methylimide (see this vol., i, 614), which melts at 89°.

T. H. P.

Synthesis of Polypeptides. III. Derivatives of Pyrrolidine-2-carboxylic Acids. Emil Fischer and Umetaro Suzuki (*Ber.*, 1904, 37, 2842—2848. Compare this vol., i, 652).—$\alpha\delta$-*Dibromovaleryl chloride*, formed by the action of phosphorus pentachloride on $\alpha\delta$-dibromovaleric acid (Willstätter and Ettlinger, Abstr., 1903, i, 362), is a colourless oil, which boils at 122—127° under 13—15 mm. pressure. $\alpha\delta$-*Dibromovalerylalanine*,

$$CH_2Br\cdot CH_2\cdot CH_2\cdot CHBr\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,$$

is formed when dibromovaleryl chloride and alanine are shaken with sodium hydroxide in aqueous solution and the product acidified. It crystallises in colourless needles, sinters at 110°, and melts at 113—116° (corr.), and is easily soluble in alcohol, ether, or benzene, moderately so in cold water. The substance may be a mixture of two isomerides. The action of ammonia on dibromovalerylalanine leads to the formation of *prolylalanine*, $\begin{matrix}CH_2\cdot CH_2\\ |\qquad\quad\\ CH_2-NH\end{matrix}>CH\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, which crystallises in colourless, glistening, microscopic plates and melts, with the formation of the anhydride, when rapidly heated at 225—230°. When heated with hydrochloric acid, it yields alanine and pyrrolidine-α-carboxylic acid. The *anhydride*, $CH_2<\begin{matrix}CH_2\cdot N\text{—}CO\cdot CHMe\\ \qquad\ |\qquad\qquad |\\ CH_2\cdot CH\cdot CO\cdot NH\end{matrix}$, crystallises in small, colourless prisms and melts at 126—129°. When heated with cupric oxide and water, the dipeptide forms a blue *copper* salt which is easily soluble in water. The anhydride does not give this reaction.

G. Y.

Pyrogenic Changes in the Pyrrole Series. Amé Pictet (*Ber.*, 1904, 37, 2792—2797).—[With A. Steinmann.]—When 1-methyl-

pyrrole is distilled through a tube heated to a dull red, it is converted into 2-methylpyrrole, which boils at 144·5—145·5° under 717 mm. pressure, has sp. gr. 0·9446 at 15°/4°, n_D 1·50353 at 16°. A small amount of pyridine was also produced.

[With G. Long.]—1-o-*Tolylpyrrole*, $C_{11}H_{11}N$, is a colourless oil which does not solidify when cooled and boils at 246°.

1-p-*Tolylpyrrole*, $C_{11}H_{11}N$, separates from dilute alcohol in pearly flakes, melts at 82°, and boils at 252° (corr.) under 728·5 mm. pressure.

1-α-*Naphthylpyrrole*, $C_{14}H_{11}N$, separates from dilute alcohol in colourless needles, melts at 42°, and boils above 360°.

1-β-*Naphthylpyrrole* separates from dilute alcohol in minute scales, melts at 170°, and boils above 360°.

2-o-*Tolylpyrrole* is an oil which boils at 284°. 2-p-*Tolylpyrrole* forms colourless flakes, melts at 153°, and boils at 294°.

2-β-*Naphthylpyrrole* forms pearly scales and melts at 155°.

[With S. Rudstein.]—1-*Benzoylpyrrole*, $C_{11}H_9ON$, prepared by the action of benzoyl chloride on potassium pyrrole, is a yellow oil, boils at 276° (corr.) under 715 mm. pressure, and is converted at a dull red heat into 2-benzoylpyrrole. T. M. L.

Bromo-derivatives of Pyrrole-2-carboxylic Acid and 1-Methylpyrrole-2-carboxylic Acid. Eugène Khotinsky and Amé Pictet (*Ber.*, 1904, 37, 2798—2802).—4 : 5-*Dibromopyrrole-2-carboxylamide*, $\begin{matrix}CBr\cdot CH\\ \|\\ CBr\cdot NH\end{matrix}\!\!>\!C\cdot CO\cdot NH_2$, prepared by the action of bromine on pyrrole-2-carboxylamide, crystallises from acetic acid in colourless flakes melting at 145—146° and containing 1 mol. of acetic acid; the hydrated amide, $C_5H_4ON_2Br_2,H_2O$, separates from hot water in colourless flakes and melts at 158°. Nitric acid oxidises the amide to dibromomaleimide.

4 : 5-*Dibromopyrrole-2-carboxylic acid*, $C_5H_3O_2NBr_2,H_2O$, prepared by heating the amide with alcoholic potash at 110—115°, crystallises from water in flakes and melts at 110°; the anhydrous acid melts at 158°.

4 : 5-*Dibromo*-1-*methylpyrrole-2-carboxymethylamide*,

$$\begin{matrix}CBr—CH\\ \|\\ CBr\cdot NMe\end{matrix}\!\!>\!C\cdot CO\cdot NHMe,$$

crystallises from dilute alcohol in long, silky needles and melts at 137°. The acid, $C_6H_5O_2NBr_2$, crystallises from alcohol in white needles, darkens and decomposes when heated, and is oxidised by nitric acid to dibromomaleic methylimide.

Bromo-1-*methylpyrrole-2-carboxymethylamide*, $C_7H_9ON_2Br$, crystallises from hot water in colourless needles and melts at 112°. The *acid*, $C_6H_6O_2NBr$, crystallises from dilute alcohol in pearly scales and decomposes without melting.

Tribromo-1-*methylpyrrole-2-carboxymethylamide*, $C_7H_7ON_2Br_3$, crystallises from dilute acetic acid or alcohol in glistening flakes and melts at 176°. The *acid*, $C_6H_4O_2NBr_3$, crystallises from alcohol in white needles and decomposes without melting. T. M. L.

Decomposition of Phenyl Esters by Organic Bases. Karl Auwers (*Annalen*, 1904, 332, 214—226).—When piperidine acts on the acetates of dibromo-*o*-hydroxybenzyl bromide and of tribromohydroxy-*m*-xylylene bromide, not only is the bromine of the side-chain replaced, but also the acyl group is removed, even when the action takes place in the presence of a solvent or at a low temperature. Such a reaction has never been observed in the case of primary bases, and investigation has shown that this decomposition depends on the strength of the secondary base and on the nature of the acyl group.

The following secondary bases were investigated: piperidine, diethylamine, piperazine, tetrahydroquinoline, and methylaniline; of these, piperidine exerts by far the most powerful action. Only when the reaction between piperidine and dibromo-*o*-acetoxybenzyl bromide takes place at $-12°$ to $-15°$ is the *dibromo-o-acetoxybenzylpiperidine*, $OAc\cdot C_6H_2Br_2\cdot CH_2\cdot C_5NH_{10}$, produced; it forms triclinic prisms melting at 86—87°. The *hydrochloride* (m. p. 222—223°) and the *hydrobromide* (decomposing at 250°) are formed when dibromo-*o*-hydroxybenzylpiperidine is warmed respectively with acetyl chloride or bromide. The benzoate, $OBz\cdot C_6H_2Br_2\cdot CH_2\cdot C_5NH_{10}$, which crystallises in needles melting at 110—111°, is obtained by benzoylating the free phenol, and can also be prepared, in contrast to the acetate, by the action of piperidine at the ordinary temperature in benzene solution on the benzoate of dibromo-*o*-hydroxybenzyl bromide; but in the absence of a solvent and at a higher temperature, dibromo-*o*-hydroxybenzylpiperidine is formed.

Diethylamine, which stands next to piperidine in activity, does not effect the hydrolysis of dibromo-*o*-acetoxybenzyl bromide in the presence of a solvent at a temperature below 40—50°, but when heated under pressure at 100°, or when the acetate is dissolved in excess of diethylamine, *dibromo-o-hydroxybenzyldiethylamine* is formed and crystallises in needles melting at 141—142°.

Methylaniline and tetrahydroquinoline are unable to effect the decomposition; when methylaniline is allowed to act on dibromo-*o*-acetoxybenzyl bromide in the absence of a solvent and at 100°, only *dibromo-o-acetoxybenzylmethylaniline*, $OAc\cdot C_6H_2Br_2\cdot CH_2\cdot NMePh$, is produced, crystallising in needles melting at 91°. In boiling xylene, tetrahydroquinoline acts in the same way, yielding *dibromo-o-acetoxybenzyltetrahydroquinoline*, which crystallises in needles melting at 105°; the free *phenol*, prepared by mixing the two components in benzene solution, crystallises in needles melting at 113—114°, and is readily acetylated.

Piperazine removes the acetyl group when it is heated with the dibromoacetoxy-derivative in boiling xylene solution, the compound $(OH\cdot C_6H_2Br_2\cdot CH_2)_2C_4N_2H_8$ being produced; it crystallises in needles melting at 199—201°. The *hydrobromide* of tetrabromodihydroxydibenzylpiperazine is precipitated on mixing solutions of dibromohydroxybenzyl bromide and piperazine, and is converted into the phenol, which forms crystals melting at 240—242°; when cautiously acetylated in the presence of pyridine it yields the acetyl derivative just mentioned, but when boiled with acetic anhydride it is converted into the diacetate of dibromosaligenin (m. p. 71°). K. J. P. O.

Complex-formation. II. Pyridine Complexes. HANS EULER (*Ber.*, 1904, 37, 2768—2773).—Determinations of the stability of pyridine metallic complexes by means of measurements of solubility and *E.M.F.* show that these complexes are much less stable than those containing ammonia or alkylamines. This is shown by the dissociation constants tabulated below:

Metal.	Pyridine.	*K.*	Ammonia.	*K.*
Ag............	$AgPy_2$	4×10^{-5}	$Ag(NH_3)_2$	5×10^{-8}
Ni............	$NiPy_2$	$2{\cdot}5 \times 10^{-1}$	$Ni(NH_3)_4$	$1{\cdot}1 \times 10^{-5}$
Cd............	$CdPy_2$	$1{\cdot}4 \times 10^{-1}$	$Cd(NH_3)_4$	$3{\cdot}2 \times 10^{-4}$
Zn............	$ZnPy_2$	$2{\cdot}8 \times 10^{-1}$	$Zn(NH_3)_4$	$1{\cdot}6 \times 10^{-3}$

T. M. L.

Thio- and Seleno-derivatives of *N*-Alkyl-pyridones and -lutidones. AUGUST MICHAELIS and A. HÖLKEN (*Annalen*, 1904, 331, 245—264).—Starting from α-halogen derivatives of pyridine, thio- and seleno-derivatives of pyridones have been prepared by the action of potassium hydrosulphide and hydroselenide. In a similar manner, the corresponding lutidones have been obtained from γ-chlorolutidines. Thus, from the methiodide of α-iodopyridine, *N*-methyl-α-selenopyridone, $\begin{matrix}CH{:}CH{\cdot}C\text{---}\\ |\qquad\quad \| \\ CH{:}CH{\cdot}NMe\end{matrix}\!\!>\!Se$, and from the methiodide of γ-chlorolutidine, *N*-methyl-γ-thiolutidone, $C\begin{matrix}\diagup\!\!\!\diagup CH{\cdot}CMe\diagdown\!\!\!\diagdown \\ \text{——}\ S\ \text{——} \\ \diagdown CH{:}CMe \diagup\end{matrix}NMe$, were respectively obtained. These substances yield alkyl iodide derivatives, which, on heating, lose alkyl iodide and are converted into methylthiol derivatives of pyridine or lutidine, isomeric with *N*-methylthio- or seleno-compounds. By the action of chlorine they are converted into trioxides analogous to the thiopyrine trioxides (compare p. 780).

(I) *Derivatives of* 1-*Methyl*-1 : 2-*pyridone*.—1 : 2-*Thio*-1-*methylpyridone*, $\begin{matrix}CH\ CH{:}C\text{---}\\ |\qquad\quad | \\ CH{:}CH{\cdot}NMe\end{matrix}\!\!>\!S$, separates when a hot concentrated solution of the methiodide of α-iodopyridine is added to the calculated quantity of 20 per cent. potassium hydrosulphide, hydrogen sulphide being at the same time evolved; it forms pale yellow needles or prisms melting at 89°, and, when boiled with concentrated hydrochloric acid, is converted into 1-methyl-1 : 2-pyridone (compare Gutbier, Abstr., 1901, i, 96). It reacts with methyl iodide, the methyl group becoming attached to the sulphur, and the iodine to the nitrogen; the *compound* forms needles melting at 155—156°; the corresponding methyl chloride *compound* forms white crystals melting at 97°. The *platinichloride* forms reddish-yellow crystals. When distilled, methyl iodide is eliminated and 2-methylthiolpyridine (m. p. 197°) formed (compare Marckwald, Klemm, and Trabert, Abstr., 1900, i, 456).

1-*Methyl*-1 : 2-*selenopyridine*, prepared in a similar manner to the sulphur compound, crystallises in brownish-yellow needles melting at 79—80°, and is less stable than the thiopyridone. The *methiodide*

crystallises in white needles melting at 186°, and the *methochloride* in needles melting at 86°; the *platinichloride* forms yellowish-brown prisms melting at 201°. When the methiodide is distilled, *a-methyl-selenolpyridine*, $CH<\begin{matrix}CH\cdot CH\\CH{=}N\end{matrix}>C\cdot SeMe$, is obtained as a colourless liquid, with an odour resembling mercaptan, boiling at 212°; it is soluble in acids and forms a very hygroscopic hydrochloride.

II. *Derivatives of* 1-*Alkyl*-1 : 4-*lutidones*.—The methiodide of γ-chlorolutidine was prepared from γ-lutidone, which was first converted into γ-chlorolutidine by Conrad and Epstein's method (Abstr., 1887, 501), and then the latter heated with methyl iodide under pressure for 6 hours at 100°; the *methiodide* crystallises with $2H_2O$ and melts at 228—230°, and, when anhydrous, at 233—234°. When γ-chlorolutidine is heated with ethyl iodide for 6 hours at 120°, the ethiodide of γ-iodolutidine is obtained as colourless leaflets melting at 239—240°.

1 : 4-*Thio*-1 : 3 : 6-*trimethylpyridine*, prepared from the methiodide just described and potassium hydrosulphide, crystallises in yellow needles melting at 267—268°. It forms a very unstable, yellow, crystalline additive *product* with sulphur dioxide. The *hydrochloride* crystallises in needles melting at 233—234°; the *methiodide* crystallises in needles melting at 236°; the *platinichloride* forms red prisms melting at 234°.

1 : 4-*Thio*-2 : 6 *dimethyl*-1-*ethylpyridine* was obtained in a similar manner to the methyl compound and forms yellow needles melting at 248°; the *methiodide* forms white crystals melting and decomposing at 154°; the *methochloride* melts at 136°. On distilling the methiodide of either of these thio-1-alkyl-lutidones, alkyl iodide is eliminated and 4-methylthiolutidine (m. p. 51°) formed, identical with the substance prepared by Marckwald (*loc. cit.*).

The *trioxide* of 1 : 4-thio-1 : 2 : 6-trimethylpyridine,

$$C\begin{matrix}\diagup CH{:}CMe\diagdown \\ -SO_2-O- \\ \diagdown CH\cdot CMe\diagup\end{matrix}NMe,2H_2O\ (?),$$

is prepared by passing chlorine into an aqueous suspension of the thiolutidine, and forms rhombic crystals, which carbonise without melting on heating and are indifferent towards both acids and alkalis.

1 : 4-*Seleno*-1 : 2 : 6-*trimethylpyridine*, prepared from the methiodide of γ-chlorolutidine and potassium selenide, crystallises in brown needles melting at 268° and is decomposed by boiling with dilute acids; the *methiodide* forms colourless needles melting and decomposing at 219°; the *methochloride* melts at 210°, and the *platinichloride*, which crystallises in red crystals, at 224°. The corresponding ethyl compound, 1 : 4-*seleno*-2 : 6-*dimethyl*-1-*ethylpyridine*, forms brownish-red needles melting at 254°; the *methiodide* crystallises in colourless needles melting at 155°, and the *methochloride* at 126°.

On distilling the methiodide of either the 1-methyl or the 1-ethyl-4-seleno-2 : 6-dimethylpyridine, 4-*methylselenol*-2 : 6-*dimethylpyridine*,

$$SeMe\cdot C<\begin{matrix}CH\cdot CMe\\CH{:}CMe\end{matrix}>N,$$

is obtained; it forms crystals melting at 70°; the *hydrochloride* melts

at 110°, and the *platinichloride*, which crystallises in brownish-red prisms, at 252°. K. J. P. O.

Carbazoles. FRITZ ULLMANN [with E. DELÉTRA and D. KOGAN] (*Annalen*, 1904, **332**, 82—104).—This paper is mainly a fuller account of work previously published (this vol., i, 270). In this communication, an account is given of the preparation of chlorocarbazoles and of naphthacarbazoles.

Carbazole, $NH<\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, is prepared by distilling phenaziminobenzoic acid with three to four times its weight of lime, and melts at 238°. 3-*Chlorocarbazole*, $NH<\begin{matrix}C_6H_3Cl\\|\\C_6H_4\end{matrix}$, is obtained thus: 4-*chloro*-2-*nitro*-1-*diphenylamine*, $NHPh\cdot C_6H_3Cl\cdot NO_2$, is prepared by heating for 10 hours 1 : 4-dichloro-2-nitrobenzene with aniline and anhydrous sodium acetate; it forms orange-red or reddish-brown crystals melting at 61°. When reduced with stannous chloride and hydrochloric acid, 4-*chloro*-2-*amino*-1-*diphenylamine* is obtained in colourless needles melting at 82°, and is converted by diazotising into 4-*chlorophenaziminobenzene*,

$$N\lessgtr\begin{matrix}NPh\\N\text{---}\end{matrix}>C_6H_3Cl,$$

which crystallises in colourless needles melting at 142°. When heated alone, it becomes 3-*chlorocarbazole*, which forms white, silvery crystals melting at 201·5°. 2-*Chlorocarbazole* is prepared by heating for 1 hour at its melting point chlorophenaziminobenzene (Ernst, Abstr., 1891, 299), and crystallises in leaflets melting at 244°; it dissolves in sulphuric acid to a yellow solution, which becomes bluish-green on addition of nitric acid.

1 : 2-*Naphthacarbazole*, $NH<\begin{matrix}C_{10}H_6\\|\\C_6H_4\end{matrix}$, prepared by the distillation of phenaziminonaphthalene (Zincke and Campbell, Abstr., 1890, 787), crystallises in colourless leaflets melting at 134·5—135° and forms colourless solutions which have a blue fluorescence; it dissolves in sulphuric acid with a yellow coloration, which becomes yellowish-green on addition of nitric acid. This compound is probably identical with the material obtained by Schöpff (Abstr., 1895, i, 107) by distilling naphthacarbazolecarboxylic acid with zinc dust, although he records the melting point as 120°. The benzoyl derivative melts at 191°. 2'-*Methyl*-1 : 2-*naphthacarbazole* is obtained from *p*-tolylnaphthylenediamine, which is converted, on diazotisation, into *p*-*tolylaziminonaphthalene*, $N\lessgtr\begin{matrix}N(C_6H_4Me)\\N\text{------}\end{matrix}>C_{10}H_6$, forming colourless crystals melting at 145°. When distilled, the compound last mentioned passes into the carbazole, which forms crystals melting at 181°; its solutions are colourless, but have a blue fluorescence; the *picrate* crystallises in red needles melting at 212°. K. J. P. O.

Constitution of Cyanine Dyes. A. MIETHE and GILBERT BOOK (*Ber.*, 1904, **37**, 2821—2824. Compare this vol., i, 622).—*Lepidine ethiodide*, $C_{10}H_{19}N,EtI$, prepared from lepidine and ethyl iodide, separates from alcohol in yellow crystals and melts at 142°.

By the action of potassium hydroxide (2 mols.) on a mixture of quinoline ethiodide (2 mols.) and lepidine ethiodide (1 mol.), diethylcyanine, $C_{23}H_{25}N_2I$, is formed as dark green needles.

The mechanism of the action is supposed to be as follows. The quinoline ethiodide is converted into a quinolone; the hydrogen eliminated in this action converts the lepidine ethiodide into its dihydro-derivative, which interacts with the quinolone, with elimination of water, to form diethylcyanine, which is thus represented:

$$\mathrm{NEtI}\Big\langle\begin{matrix}\text{—}C_6H_4\text{—}\\ CH\cdot CH_2\end{matrix}\Big\rangle CH\cdot CH{:}C\Big\langle\begin{matrix}C_6H_4\cdot NEt\\ CH{=\!=}CH\end{matrix}.$$

Di-iododiethylcyanine, $C_{23}H_{25}N_2I_3$, prepared by the action of iodine on diethylcyanine, separates from alcohol in olive-green, glistening crystals. It is not a periodide. A. McK.

Preparation and Transformations of Members of the Tetrahydrocarbazole Series.

GIUSEPPE PLANCHER and O. CARRASCO (*Atti R. Accad. Lincei*, 1904, [v], 13, i, 632—636. Compare Plancher and Testoni, Abstr., 1900, i, 562).—On condensation with alcoholic zinc chloride, menthone phenylhydrazone yields:

(1) 3-*Methyl*-6-iso*propyl*-Δ^N-*carbazolenine*,

$$\begin{array}{l} CH{:}CH\cdot C\text{——}CPr^{\beta}\cdot CH_2\cdot CH_2 \\ CH{:}CH\cdot C\cdot N{:}C\cdot CH_2\text{——}CHMe \end{array},$$

which forms a colourless mass boiling at 170—171° under 14 mm. pressure, and crystallises when strongly cooled. Its *picrate*,

$$C_6H_{21}N,C_6H_2(NO_2)_3\cdot OH,$$

is pale yellow and melts at 166—167°. Its *methiodide* separates from a mixture of alcohol and ether in crystals melting and decomposing at 209—210°. Digestion of the methiodide with silver chloride yields the methochloride, which gives a crystalline aurichloride and platinichloride.

(2) 4-*Methyl*-1-iso*propyltetrahydrocarbazole*,

$$\begin{array}{l} CH{:}CH\cdot C\text{———}C\cdot CHMe\text{–}CH_2 \\ CH{:}CH\cdot C\cdot NH\cdot C\cdot CHPr^{\beta}\cdot CH_2 \end{array},$$

which boils at 202—204° under 14 mm. pressure in a slightly impure state and yields a dark red *picrate* melting at 164—165°.

The condensation of β-methylketo*cyclo*hexanephenylhydrazone by means of alcoholic sulphuric acid yields either 4- or 2-*methyltetrahydrocarbazole*,

$$\begin{array}{l} CH{:}CH\cdot C\text{———}C\cdot CHMe\cdot CH_2 \\ CH{:}CH\cdot C\cdot NH\cdot C\cdot CH_2\text{—}CH_2 \end{array} \quad \text{or}$$

$$\begin{array}{l} CH{:}CH\cdot C\text{———}C\cdot CH_2\cdot CH_2 \\ CH{:}CH\cdot C\cdot NH\cdot C\cdot CH_2\cdot CHMe \end{array},$$

which gives well-formed rhombic crystals melting at 98—99°; it has no basic properties, smells faintly of indole, gives a red picrate, but does not give Angeli's reaction with anhydrous oxalic acid. With methyl iodide it gives the hydriodide of a base,

$$\begin{array}{l} CH{:}CH\cdot C\text{———}CMe\cdot CH_2\cdot CH_2 \\ CH{:}CH\cdot C\cdot NMe\cdot C{:}CH\text{——}CHMe \end{array},$$

which yields a *picrate*, $C_{15}H_{19}N,C_6H_2(NO_2)_3OH$, crystallising in pale yellow leaflets melting at 143—144°. With chloroform, in presence

of sodium ethoxide, the 4- or 2-methyltetrahydrocarbazole gives a *base*,

$$\begin{array}{l} CH:CH\cdot C\text{——}C(CHCl_2)\cdot CH_2\cdot CH_2 \\ CH:CH\cdot C\cdot N:C\cdot CH_2\text{————}CHMe \end{array} \quad \text{or} \quad \begin{array}{l} CH:CH\cdot C\text{——}C(CHCl_2)\cdot CHMe\cdot CH_2 \\ CH:CH\cdot C\cdot N:C\cdot CH_2\text{————}CH_2 \end{array},$$

which separates from light petroleum in very pale yellow plates melting at 125—126° and yields a *picrate* melting and decomposing at 162—163°.

4- or 2-Methyltetrahydrocarbazole is readily reduced by phosphorus and hydriodic acid to the corresponding 4- or 2-*methylcarbazoline*, $C_{13}H_{17}N$, which is obtained in colourless, pleasant-smelling crystals melting at 102—103°; its *hydrobromide* melts at 230—231° and its *hydriodide* at 227—229°; its *platinichloride*, $(C_{13}H_{17}N)_2,H_2PtCl_6$, was analysed. T. H. P.

Oxidation Products from *p*-Phenylenediamine. I. ERNST ERDMANN (*Ber.*, 1904, 37, 2776—2780).—When *p*-phenylenediamine is oxidised with potassium permanganate, the chief products are ammonia and carbon dioxide, $C_6H_8N_2 + 13O = 6CO_2 + 2NH_3 + H_2O$, but oxalic acid and hydrogen cyanide are also produced in small quantities. T. M. L.

Action of Phthalic Anhydride on Aromatic Diamines. GUSTAV KOLLER (*Ber.*, 1904, 37, 2880—2883).—Phthalyl-4:4′-diaminodiphenyl, and not diphthalyliminodiphenyl (Bandrowski, Abstr., 1884, 1015), is formed when phthalic anhydride and benzidine are boiled in aqueous suspension. *Phthalyl*-4 : 4′-*diaminodiphenyl*,

$$C_6H_4{<}\begin{array}{l} CO\cdot NH\cdot C_6H_4 \\ CO\cdot NH\cdot C_6H_4 \end{array},$$

separates from its solution in boiling nitrobenzene in yellow, granular crystals, melts above 300°, and is insoluble in aqueous alkali hydroxides or dilute acids. When acted on by potassium nitrate in concentrated sulphuric acid solution, it yields a *mononitro*-derivative which crystallises in yellow needles, melts at 225°, and is hydrolysed by boiling aqueous sodium carbonate solution to 3-*nitro*-4′-*phthalamino*-4-*aminodiphenyl*, $NH_2\cdot C_6H_3(NO_2)\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$. This crystallises in orange-coloured needles, melts at 140°, is easily soluble in aqueous sodium carbonate, and is hydrolysed by concentrated ammonia to *o*-nitrobenzidine, which crystallises in red needles and melts at 190°. G. Y.

Ethyl αβ-Diacylpropionates and Primary Hydrazines. WALTHER BORSCHE and M. SPANNAGEL (*Annalen*, 1904, 331, 298—318).—The action of hydrazine and primary hydrazines on ethyl αβ-diacylpropionates, $RCO\cdot CH_2\cdot CH(COR)\cdot CO_2Et$, has been investigated, the action of phenylhydrazine on ethyl phenacylacetoacetate, on ethyl acetonylacetoacetate, and on ethyl phenacylbenzoylacetate being described in this communication.

When phenylhydrazine and ethyl phenacylacetoacetate are brought

together in alcoholic solution, the *monophenylhydrazone* of the ester, $NHPh\cdot N{:}CPh\cdot CH_2\cdot CHAc\cdot CO_2Et$ or

$$COPh\cdot CH_2\cdot CH(CMe{:}N\cdot NHPh)\cdot CO_2Et,$$

separates in white needles melting at 152°; the hydrazone is unstable, and, even in the pure state, when exposed to light becomes yellow, acquires an unpleasant odour, and gradually becomes a brown, oily mass; it gives no colour reaction with ferric chloride in alcoholic solution, and does not react either with phenylhydrazine or semicarbazide. After long heating in alcoholic solution, 1 mol. of water is lost and a ring is formed, *ethyl* 1 : 5-*diphenyl*-2-*methyl*-$\Delta^{2:5}$-*dihydropyridazine*-3-*carboxylate*, $N\lessgtr\begin{matrix}CPh-CH_2\\NPh\cdot CMe\end{matrix}\gtrless C\cdot CO_2Et$, being produced; it forms colourless crystals melting at 114—116°; the hydrazone is more rapidly changed into the pyridazine either by warming with acetic anhydride or by heating at 166—170°. The corresponding *acid* is obtained by hydrolysing the ester just described or by hydrolysing the hydrazone, and forms small crystals melting at 185—186°; if the ester of the pyridazine is fused with potassium hydroxide, aniline is eliminated, a methyl group oxidised, 2-*phenylpyrrole*-4 : 5-*dicarboxylic acid* being produced, $\begin{matrix}C(CO_2H)\cdot CH\\ \| \\ C(CO_2H)\cdot NH\end{matrix}\!\!>CPh$; it crystallises in needles melting at 250°.

Ethyl phenacylacetoacetate and semicarbazide yield a cyclic semicarbazone, *ethyl* 5-*phenyl*-2-*methyl*-$\Delta^{2:5}$-*dihydropyridazine*-1-*carbonamide*-3-*carboxylate*, $CPh\lessgtr\begin{matrix}CH_2\cdot C(CO_2Et)\\N\cdot N(CO\cdot NH_2)\end{matrix}\gtrless CMe$, which crystallises in needles melting at 254·5°; it does not yield an acetyl derivative, and when warmed with alkali hydroxide the carbethoxy-group is alone hydrolysed, an *amide acid* being formed; it is crystalline and melts and decomposes at 247—248°. When the ester amide is boiled with aniline, *ethyl phenylmethyldihydropyridazinecarbonanilidecarboxylate*,

$$C_{21}H_{21}O_3N_3,$$

is obtained as colourless crystals melting at 192°; it is also formed when ethyl phenacylacetoacetate is condensed with phenylsemicarbazide.

Ethyl acetonylacetoacetate forms with phenylhydrazine a viscid oil. Semicarbazide and the ester condense, 2 mols. of water being eliminated and *ethyl* 2 : 5-*dimethyl*-$\Delta^{2:5}$-*dihydropyridazine*-1-*carbonamide*-3-*carboxylate*, $CMe\lessgtr\begin{matrix}CH_2\cdot C(CO_2Et)\\N\cdot N(CO\cdot NH_2)\end{matrix}\gtrless CMe$, produced; it forms colourless crystals melting at 230°.

Ethyl phenacylbenzoylacetate (m. p. 69—72°; Paal, *Ber.*, 1888, 21, 1485, gives the melting point as 55—58°) reacts slowly with phenylhydrazine, yielding no definite products; semicarbazide gives a normal *semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N{:}CPh\cdot CH_2\cdot CHAc\cdot CO_2Et$, which crystallises in colourless needles melting at 138—140°.

Ethyl benzoylacetate reacts readily with semicarbazide, yielding 3-*phenylpyrazolone*-1-*carbonamide*, $\begin{matrix}CPh=N\\ | \\ CH_2\cdot CO\end{matrix}\!\!>N\cdot CO\cdot NH_2$, which forms crystals melting at 184—185°. K. J. P. O.

1-Phenyl-3-methylthiopyrazolone. AUGUST MICHAELIS and ROB. PANDER (*Ber.*, 1904, **37**, 2774—2775).—*1-Phenyl-3-methyl-5-thiopyrazolone*, $\begin{matrix}CH{:}C(SH)\\ | \\ CMe{:}N\end{matrix}\!>\!NPh$, prepared by hydrolysing the benzoyl derivative with dilute hydrochloric acid at 120°, separates from alcohol in well-formed crystals, melts at 109°, and boils with much decomposition at 294°. Methyl iodide reconverts it at once into the methiodide of thioantipyrine. The *benzoyl* derivative, $\begin{matrix}CH{:}C(SBz)\\ | \\ CMe{=\!=}N\end{matrix}\!>\!NPh$, was obtained by distilling the thioantipyrine benzoyl chloride,

$$\begin{matrix}CH{=\!=}C(SBz)\\ | \\ CMe{:}N(MeCl)\end{matrix}\!>\!NPh$$

(Abstr., 1902, i, 316), when a part of the methyl chloride is split off, whilst part of the substance is decomposed into benzoyl chloride and ψ-thioantipyrine; it crystallises from light petroleum in minute, white needles and melts at 93°. T. M. L.

Thiopyrine Series. AUGUST MICHAELIS [with ALBERT BESSON, WILLY MOELLER, and MAX KOBER] (*Annalen*, 1904, **331**, 197—244. Compare Abstr., 1901, i, 52).—Thiopyrine [thioantipyrine; 1-phenyl-2 : 3-dimethyl-2 : 5-thiopyrazole] is prepared by passing a current of carbon disulphide into a solution of sodium, potassium, or ammonium hydrosulphide, and adding later, or at the same time, a hot or cold aqueous or alcoholic solution of the methochloride or methiodide of phenylmethylchloropyrazole. It may also be obtained by treating an aqueous solution of antipyrine chloride with sodium thiosulphate, finally heating on the water-bath. The reactions may be represented as follows: $C_{11}H_{12}N_2Cl_2 + Na_2S_2O_3 + H_2O = H_2SO_4 + 2NaCl + C_{11}H_{12}N_2S$, and $Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + SO_2 + S + H_2O$.

When distilled under the ordinary or reduced pressure, thiopyrine is converted into ψ-thiopyrine (5-methylthiol-1-phenyl-3-methylpyrazole), whereas antipyrine is, at higher temperatures, more stable than its isomeride. In physiological action, the two substances are alike.

Thiopyrine hydriodide forms transparent crystals sintering at 194° and melting at 202°, and on distillation changes into the hydriodide of the ψ-thiopyrine, which melts at 174—175°. The *ethiodide* forms thick plates melting at 158°; the iso*propyliodide*, $C_{11}H_{12}N_2S,Pr^{\beta}I,H_2O$, forms white crystals, melting, when anhydrous, at 170—172°, and yielding, when distilled, 5-*iso*propylthiol-1-phenyl-3-methylpyrazole. The iso*butyliodide* forms crystals melting at 117°, and the *allyliodide* crystals melting at 125°. The *benzylchloride* is an oil, and the corresponding *iodide* forms white needles melting at 174—175°.

Both methylene and ethylene iodides act readily on thiopyrine, forming respectively bis-compounds, thus: $CH_2\left[S{\cdot}C\!\lessdot\!\begin{matrix}NPh{\cdot}N\\ \quad\ \ \| \\ CH-CMe\end{matrix}\right]_2$. The *methiodide* of 5-*methylenebis*-1-*phenyl*-3-*methylthiopyrazole* forms white needles melting and decomposing at 197°, the *methochloride* is crystalline and melts at 201°. The *methobromide* of 5-*ethylenebis*-

1-*phenyl*-3-*methylthiopyrazole* is crystalline and hygroscopic and melts at 176°.

Thiopyrine trioxide, $\begin{array}{l}\mathrm{CMe{:}NMe{\cdot}O}\\ \big|\quad\ \ \mathrm{NPh}\ \big|\\ \mathrm{CH{=}CH{-}SO_2}\end{array}$, is prepared by heating antipyrine chloride with sodium sulphite and crystallises in needles (with H_2O) from water.

Homologues of Thiopyrine.—*Ethylthiopyrine* (2 : 5-*thio*-1-*phenyl*-3-*methyl*-2-*ethylpyrazole*), $\begin{array}{l}\mathrm{CMe{:}NEt}\\ \big|\quad\ \ \mathrm{NPh}\!>\!\mathrm{S}\\ \mathrm{CH{=}C{-}{-}{-}}\end{array}$, is prepared from the ethiodide of 5-iodo-1-phenyl-3-methylpyrazole, which is converted first into the ethochloride and then treated with potassium hydrosulphide in alcoholic solution (compare Michaelis and Pasternack, Abstr., 1899, i, 941, and Michaelis and Bindewald, Abstr., 1901, i, 52); it forms crystals melting at 171°, behaves towards ferric chloride as does thiopyrine, and with sulphur dioxide forms an *additive product*, $C_{12}H_{14}N_2S,SO_2$, crystallising in yellow leaflets which melt and decompose at 113°. The *methiodide* forms crystals melting at 203°.

Ethylthiopyrine trioxide (*ethylammonium* 1-*phenyl*-3-*methyl*-2 : 5-*pyrazolesulphonate*), $\begin{array}{l}\mathrm{CMe{:}NEt{\cdot}O}\\ \big|\quad\ \ \mathrm{NPh}\,\big|\\ \mathrm{CH{=}C{-}{-}SO_2}\end{array}$, is formed when chlorine is passed into an aqueous solution of ethylthiopyrine, and crystallises in leaflets melting and decomposing at 257°.

The *allylbromide* of 5-*bromo*-1-*phenyl*-3-*methylpyrazole* is obtained by heating chloropyrazole with allyl bromide under pressure, and forms colourless needles melting at 196°; the corresponding *allylchloride* is hygroscopic and melts at 182°. The *allyliodide* of 5-iodo-1-phenyl-3-methylpyrazole crystallises in needles melting at 203°, and the corresponding *allylchloride* forms crystals melting at 193—194°. *Allylthiopyrine*, prepared from the allylchloride, forms crystals melting at 123°, and, when treated with sulphur dioxide, yields a crystalline *additive* product melting at 92—95°; the *methiodide* forms crystals melting at 142°. By aqueous chlorine, allylthiopyrine is converted into *chloropropylthiopyrine trioxide*, $\begin{array}{l}\mathrm{C{-}{-}NPh}\diagdown\\ \|\quad\ \mathrm{O{\cdot}SO_2{\cdot}N{\cdot}CH_2{\cdot}CHMeCl}\\ \mathrm{CH{-}CMe}\diagup\!\!\diagup\end{array}$, which forms crystals melting and decomposing at 244°.

Methylthiopyrine (2 : 5-*thio*-1-*phenyl*-2 : 3 : 4-*trimethylpyrazole*) forms monoclinic crystals melting at 129°; the *hydrochloride* is very hygroscopic, and the *platinichloride* (with $2H_2O$) is a flesh-coloured powder melting at 226° (compare Abstr., 1902, i, 315). It forms two *additive* products with sulphur dioxide; at the ordinary temperature, an orange-yellow, crystalline precipitate melting at 145—148°, and at 100° greenish-yellow, stable crystals, $C_{12}H_{14}N_2S,SO_2,H_2O$, melting at 200—203°. The *methiodide* forms large, monoclinic crystals melting at 167°, which crystallise from water with H_2O. The *methochloride* crystallises in needles melting at 91°, and yields a *platinichloride* which

crystallises in reddish-brown leaflets melting at 256°. The *ethiodide* crystallises in colourless plates melting at 125°, and the *benzylchloride* forms crystals melting at 72°.

Methylthiopyrine trioxide (*methylammonium* 1-*phenyl*-3 : 4-*dimethylpyrazolesulphonate*), $\begin{array}{l}\mathrm{CMe{:}NMe{\cdot}O}\\ \mid\quad\ \mathrm{NPh}\quad\mid\\ \mathrm{CMe{:}C{-\!\!-}SO_2}\end{array}$, forms transparent, rhombic crystals melting and decomposing at 305°.

Dichloromethylthiopyrine crystallises in hygroscopic, yellow needles, and the *dibromide* is a yellowish-red powder melting at 111°.

Pseudothiopyrines.—On heating the iodoalkyl derivatives of thiopyrines, two decompositions take place: alkyl iodide is eliminated and a 5-thioalkylpyrazole formed; and secondly, especially in the case of ethylthiopyrine, ethyl iodide is eliminated and a ψ-thiopyrine produced, thus:

$$\begin{array}{l}\mathrm{CMe{:}N(MeI)}\\ \mathrm{CH{=}C(SEt)}\end{array}\!\!>\mathrm{NPh} = \mathrm{EtI} + \left|\begin{array}{l}\mathrm{CMe{:}NMe}\\ \quad\ \ \mathrm{S}\\ \mathrm{CH{=}C{-\!\!-}}\end{array}\right.\!\!>\mathrm{NPh},\ \text{or}\ \begin{array}{l}\mathrm{CMe{\equiv\!\equiv}N}\\ \mathrm{CH{:}C(SMe)}\end{array}\!\!>\mathrm{NPh}.$$

The ψ-thiopyrines yield characteristic methiodides, are converted by oxidising agents into sulphones, and with halogen give additive products if a hydrogen atom is present in position 4; if an alkyl group occupies position 4, the group (SMe) is replaced by halogen. By a mixture of nitric and sulphuric acids, the phenyl group is nitrated. Concentrated hydrochloric acid causes the elimination of sulphur and methyl chloride and the formation of a pyrazole.

ψ-*Thiopyrine* (5-*methylthiol*-1-*phenyl*-3-*methylpyrazole*), best prepared by the repeated distillation of thiopyrine, is a colourless liquid of pleasant odour boiling at 165—166° under 11 mm. and at 306—307° under 760 mm. pressure; the *hydrochloride* forms crystals with H_2O, is decomposed by water, and when dry melts at 103°. The *platinichloride* forms with $2H_2O$ red crystals melting at 160°. The *nitrate* forms hygroscopic crystals melting at 53—55°, and the *picrate* yellow needles melting at 77—78°. ψ-Thiopyrine only combines with alkyl iodides when heated under pressure; the methiodide is identical with that obtained from thiopyrine; the *ethiodide* forms white needles, the iso*propiodide* crystals with H_2O, which melt when anhydrous at 187°, and the iso*butyliodide* colourless crystals melting at 189—191°.

The *sulphone* of ψ-thiopyrine (1-*phenyl*-3-*methyl*-5-*methylsulphonepyrazole*), $\begin{array}{l}\mathrm{CMe{\equiv\!\equiv}N}\\ \mathrm{CH{:}C(SO_2Me)}\end{array}\!\!>\mathrm{NPh}$, is obtained when ψ-thiopyrine, dissolved in acetic acid, is oxidised by potassium permanganate, dilute nitric acid, or hydrogen peroxide; it crystallises in needles melting at 89—90°. The *methiodide* forms crystals melting at 194°.

4-*Bromo*-ψ-*thiopyrine* (4-*bromo*-5-*methylthiol*-1-*phenyl*-3-*methylpyrazole*), prepared by brominating ψ-thiopyrine in chloroform solution, crystallises in plates melting at 52°, and is also formed from 4-bromothiopyrine. The *methiodide* forms crystals melting at 179°, and when heated with dilute sodium hydroxide yields mercaptan and antipyrine.

The corresponding *sulphone*, 4-*bromo*-1-*phenyl*-3-*methyl*-5-*methylsulphonepyrazole*, crystallises in white leaflets melting at 150—151°.

Nitro ψ-*thiopyrine*, prepared by treating ψ-thiopyrine with a mixture of nitric and sulphuric acids, crystallises in pale yellow leaflets melting at 135—136°.

Homo-ψ-*thiopyrine*, $\begin{array}{l}CH{=\!=\!=}N \\ | \\ CH{:}C(SMe)\end{array}\!\!>NPh$, is obtained as a yellow oil boiling at 142—143° under 14 mm. pressure, when the methiodide of homothiopyrine is distilled.

When the ethiodide of thiopyrine is distilled under the ordinary pressure, the distillate contains methyl and ethyl iodides, and a mixture of ψ-thiopyrine and ethyl-ψ-thiopyrine. The methiodide of methylthiopyrine behaves similarly. *Ethyl*-ψ-*thiopyrine* (5-*ethylthiol*-1-*phenyl*-3-*methylpyrazole*), prepared by distilling methylthiopyrine at first under reduced pressure and then under the ordinary pressure, is a colourless oil boiling at 178° under 19—20 mm. and at 308—310° under 760 mm. pressure. The *methiodide* melts at 158°, and the *sulphone*, which crystallises in leaflets, at 61—62°. iso*Propyl*-ψ-*thiopyrine* (5-iso*propylthiol*-1-*phenyl*-3-*methylpyrazole*), prepared from the *iso*propiodide of thiopyrine, boils at 308—310° under 760 mm. pressure; the *methiodide* crystallises with H_2O, and when anhydrous melts at 170—171°; the *sulphone* forms needles melting at 83°. iso*Butyl*-ψ-*thiopyrine* (5-iso*butylthiol*-1-*phenyl*-3-*methylpyrazole*) is an oil boiling at 313—314° under 760 mm. pressure; the corresponding *allyl* derivative is crystalline, melting at 56—57° and boiling at 184—188° under 11 mm. pressure; no sulphone was formed on oxidation.

Benzyl-ψ-*thiopyrine* (5-*benzylthiol*-1-*phenyl*-3-*methylpyrazole*) is obtained when the benzyl-chloride or -iodide of thiopyrine is distilled under the lowest possible pressure, and forms a colourless oil boiling at 246° under 20 mm. pressure; the methiodide is identical with the benzyliodide of thiopyrine. The *sulphone* forms colourless needles melting at 92°.

Methyl-ψ-*thiopyrine* (5-*methylthiol*-1-*phenyl*-3 : 4-*dimethylpyrazole*),

$$\begin{array}{l}CMe{=\!=\!=}N \\ | \\ CMe{:}C(SMe)\end{array}\!\!>NPh,$$

obtained by distilling either methylthiopyrine or the methiodide, forms plate-like, triclinic crystals melting at 56° and boiling at 179° under 15 mm. and at 310° under 760 mm. pressure. The methylthiol group is eliminated either by heating with hydrochloric acid or by reducing with sodium amalgam; with the first reagent, 1-*phenyl*-3 : 4-*dimethylpyrazole* (b. p. 277—278°) is formed, whilst in the latter case 1-phenyl-3 : 4-dimethylpyrazoline is produced. When treated with bromine, the methylthiol group is replaced by bromine, 5-bromo-1-phenyl-3 : 4-dimethylpyrazole being formed. The *hydrochloride* of methyl-ψ-thiopyrine crystallises in needles melting at 108°, and the *platinichloride* crystallises with $2H_2O$ in yellowish-red leaflets melting at 203°. The *sulphone* crystallises in needles melting at 137° and can be sublimed; its *methiodide* forms crystals melting at 188°, its *methochloride* melts at 81°, and the *platinichloride*, which crystallises in brown leaflets, melts and decomposes at 225°. On heating the sulphone with bromine under

pressure for five hours at 110°, 1-*bromophenyl*-3 : 4-*dimethyl*-5-*methylsulphonepyrazole* is formed, and crystallises in needles melting at 178°.

When the ethiodide of methylthiopyrine is distilled, methyl iodide is eliminated and 5-*ethylthiol*-1-*phenyl*-3 : 4-*dimethylpyrazole* produced; it is a viscid, colourless oil boiling at 180—185° under 15 mm. and at 316—318° under 760 mm. pressure. The *sulphone* forms needles melting at 115°. At the same time a small quantity of ethyl iodide is formed together with 5-thiomethylpyrazole, which separates as crystals.

K. J. P. O.

Condensation of *o*-Phenylenediamine with Phthalonic Acid. Camillo Manuelli and G. Silvestri (*Gazzetta*, 1904, **34**, i, 493—500).—When heated either directly at 180—200° or in alcoholic solution in a reflux apparatus, a mixture of *o*-phenylenediamine and phthalonic acid yields a *quinoxaline* derivative, $C_6H_4<\begin{matrix} N{:}C\cdot C_6H_4\cdot CO_2H \\ N{:}\dot{C}\cdot OH \end{matrix}$, which crystallises from alcohol or ethyl acetate in shining, white laminæ, melting and decomposing at 232°, and is soluble in alkali solutions from which it is precipitated by mineral acids. By concentrated hydrochloric or 50 per cent. sulphuric acid it is partially dissolved, both the dissolved and insoluble portions becoming yellow with formation of an apparently tautomeric form, which is only stable in presence of strong acids, and is converted into the original compound by water. The *barium* salt ($+10H_2O$) and the *ammonium* salt crystallise in white needles; the *o-phenylenediamine* salt crystallises from alcohol in pale yellow plates melting and decomposing at 203°. When heated either with acetic anhydride or with excess of acetic chloride as long as hydrogen chloride is evolved, the acid yields the corresponding *lactone*, $C_6H_4<\begin{matrix} N{:}C\text{——}C_6H_4 \\ N{:}\dot{C}\cdot O\cdot \dot{C}O \end{matrix}$, which crystallises from alcohol in fan-shaped aggregates of slender, white needles or from benzene in separate needles, gradually changing into prisms, and melts at 201—203°; it dissolves in dilute potassium hydroxide solution and the benzene solution is fluorescent. With alcoholic ammonia, the lactone gives rise to a derivative of *pyridine*, $C_6H_4<\begin{matrix} N{:}C\text{———}C_6H_4 \\ N{:}\dot{C}\cdot NH\cdot \dot{C}O \end{matrix}$, which crystallises from alcohol in slender, pale yellow needles melting at 266°. The corresponding *platinichloride* was prepared and analysed.

T. H. P.

Condensations of Phenols and Aromatic Amines with Benzylideneaniline. Charles Mayer (*Compt. rend.*, 1904, **138**, 1612—1613).—Benzylideneaniline condenses with α-naphthylamine in acetic acid solution to form a compound $C_{48}H_{34}N_2$, melting at 223°, crystallising in yellow, prismatic crystals, unchanged by boiling acid or alkali solutions, and giving no benzoyl derivative; it is probably 1 : 2 : 4 : 5-*tetraphenyl*-3 : 6-*dinaphthyldihydropyrazine*,

$$C_{10}H_7\cdot N<\begin{matrix} CPh{:}CPh \\ CPh{:}CPh \end{matrix}>N\cdot C_{10}H_7.$$

Benzylideneaniline condenses with α-naphthol to form a compound, $C_{30}H_{23}ON$, in the form of orange crystals melting at 158°, and identical with the 1 : 2 : 3-triphenyl-4 : 2-α-naphtho*iso*oxazine obtained by Betti from the condensation of α-naphthol, benzaldehyde, and aniline (compare Abstr., 1901, i, 81, 611).

Benzylideneaniline forms with resorcinol a white, crystalline compound which becomes brick-red at 120° and deep green at 300°, and does not contain nitrogen. M. A. W.

Additive Hydrogen Chloride Compounds of Rosaniline Salts; their Dissociation, Thermo-chemistry, and Constitution. JULES SCHMIDLIN (*Compt. rend.*, 1904, 138, 1615—1617. Compare this vol., i, 698).—The formation of a white heptahydrochloride by the absorption of hydrogen chloride at the temperature of liquid air by the coloured trihydrochloride of rosaniline and its homologues is a reversible reaction, for if the white compound is sealed in a tube at the ordinary temperature, hydrogen chloride is evolved and the colour becomes successively yellow, orange, red, brown, and finally the black colour of the trihydrochloride, whilst the effect of heating the latter salt is to convert it into the monohydrochloride. From thermo-chemical considerations it appears that the first mol. of HCl absorbed by pararosaniline or by hexamethylpararosaniline trihydrochloride is in the form of a solution, the rest forming an integral part of the molecule, and the white compounds, which are the final products, and correspond with the absorption of 8 mols. of HCl, must be regarded as heptahydrochlorides holding 1 mol. of HCl in solution. Representing the coloured trihydrochloride by the quinonoid formula,

$$HCl,NH{:}C{<}{}^{CH:CH}_{CH:CH}{>}C{:}C(C_6H_4{\cdot}NH_2,HCl)_2,$$

the formula suggested for the colourless heptahydrochloride or tetrachloro*cyclo*hexanerosaniline trihydrochloride is

$$HCl,NH_2{\cdot}CCl{<}{}^{CH_2{\cdot}CHCl}_{CH_2{\cdot}CHCl}{>}CCl{\cdot}CH(C_6H_4{\cdot}NH_2,HCl)_2.$$

M. A. W.

Additive Compounds of Ammonia and Rosaniline. JULES SCHMIDLIN (*Compt. rend.*, 1904, 138, 1709—1711. Compare this vol., i, 698).—Prud'homme and Rabaut (compare Abstr., 1893, i, 640) have already observed that rosaniline salts absorb 2 mols. of dry ammonia to form a carmine-red compound; the author, however, finds that at −15° pararosaniline monohydrochloride absorbs 3·9 mols., and at −23° hexamethylpararosaniline monohydrochloride absorbs 4 mols. of ammonia to form colourless compounds, which in a vacuum give up the absorbed ammonia and revert to the original salts. In the case of pararosaniline monohydrochloride, the heat development accompanying the absorption of the first molecule of ammonia is 5·6 Cal., and of the second 4·9 Cal., the corresponding values for the hexamethylpararosaniline salt are 8·4 Cal. and 7·0 Cal. respectively. The author concludes that rosaniline salts are unsaturated compounds, capable of absorbing equivalent quantities of either acids or bases to form saturated colourless compounds, and, assuming the quinonoid formula,

$C(C_6H_4 \cdot NH_2)_2:C<{CH:CH \atop CH:CH}>C:NH \cdot HCl$, for the unsaturated salt, the formula for the saturated ammonium compound would be $CH(C_6H_4 \cdot NH_2)_2 \cdot C(NH_2)<{CH(NH_2) \cdot CH_2 \atop CH(NH_2) \cdot CH_2}>C(NH_2)_2HCl$.

M. A. W.

Dibenzylideneacetone and Triphenylmethane. V. ADOLF BAEYER and VICTOR VILLIGER (*Ber.*, 1904, 37, 2848—2880. Compare Abstr., 1902, i, 380, 769; 1903, i, 811; this vol., i, 308, 454).—The authors propose the name fuchsone for diphenylquinomethane (Bistrzycki and Herbst, Abstr., 1903, i, 639) as the basis of a general nomenclature. The phenylimine, $CPh_2:C<{CH:CH \atop CH:CH}>C:NPh$, is termed fuchsonephenylimine, its hydrochloride is fuchsonephenylimonium chloride, aurin is dihydroxyfuchsone, aniline blue, diphenylaminofuchsonephenylimonium chloride, &c.

Condensation of benzophenone chloride with dimethylaniline in presence of zinc chloride leads to the formation of p-*dimethylaminotriphenylcarbinol*, which crystallises in sheaves of colourless needles and melts at 92—93°. With picric acid, it forms the insoluble red *picrate* of fuchsonedimethylimonium, which crystallises in prisms. The *oxalate*, $C_{21}H_{21}ON,C_2H_2O_4$, crystallises in white leaflets.

p-Methylaminotriphenylmethane, formed, along with a crystalline tertiary *base*, from methylaniline and benzhydrol, is best purified by conversion into its hydrochloride. The *carbinol*,

$$NHMe \cdot C_6H_4 \cdot CPh_2 \cdot OH,$$

is obtained from the leuco-base by acetylation, oxidation with manganese dioxide and sulphuric acid, and hydrolysis of the *acetylmethylaminotriphenylcarbinol* formed. The *picrate* crystallises in orange-coloured leaflets or red needles.

Diacetyl-p-*diaminotriphenylmethane*, obtained by heating p-diaminotriphenylmethane with acetic anhydride, crystallises in needles, melts at 233—234°, and is oxidised by manganese dioxide and sulphuric acid to *diacetyl*-p-*diaminotriphenylcarbinol*, which crystallises in red prisms, melts at 266—267°, and dissolves in concentrated sulphuric acid or warm glacial acetic acid to red solutions. The carbinol, obtained by hydrolysis of its diacetyl derivative, is best purified by conversion into its *picrate*, which crystallises in black prisms, and from that into its *methyl* ether, which crystallises in colourless plates and melts at 161—163°. When boiled with hydrochloric acid, the methyl ether yields *aminofuchsoneimonium chloride*, $C_6H_4NH_2 \cdot CPh:C_6H_4:NH_2Cl$, which forms yellowish-green crystals; the *nitrate* is yellowish-green, the *oxalate* is blue. *Di*-p-*aminotriphenylcarbinol*, obtained from the chloride by the action of barium carbonate in aqueous solution, crystallises in pointed prisms, melts, when slowly heated, at 167—168°, when rapidly heated from 160°, at 173—175°, decomposes immediately above its melting point, and commences to lose water on prolonged heating at 140°. *Aminofuchsoneimine*, the base of Doebner's violet, is obtained by shaking its salts with sodium hydroxide, water, and benzene. The benzene solution closely resembles that of the colour-base

of magenta, but is more stable. After some days, it deposits an amorphous polymerisation product, which is also obtained from the carbinol on heating at 180° in a current of hydrogen, and which sinters above 250°.

p Phenylaminofuchsonephenylimine, the colour-base of viridine (compare Meldola, Trans., 1882, 41, 187), is formed when dianisylphenylcarbinol, aniline, and benzoic acid are heated together. It crystallises in brown, transparent plates and melts at 166—168°. The *picrate* crystallises in bronze, rhombic plates. The salts of *p*-phenylaminofuchsonephenylimoniums form green solutions; the chloride crystallises in needles; the sulphate crystallises in golden, rhombic plates or prisms, the *nitrate* in prisms.

The colour-base of magenta is soluble in water or dilute aqueous sodium hydroxide and may be extracted with benzene or ether; on adding more concentrated sodium hydroxide, the base is salted out. It combines easily with methyl alcohol to form the methyl ether of the carbinol, and with aniline to yield anilide, but more slowly with ethyl alcohol or water. The action of sodium hydroxide on paramagenta and of heat on the carbinol lead to the formation of substances which may be polymerisation products of the fuchsoneimine or the anhydride of the carbinol. By replacement of the methoxyl groups of tri-*p*-anisylcarbinol by aniline, a pure triphenylpararosaniline has been obtained. This gives a characteristic, insoluble, crystalline picrate. Diphenylamine-blue probably contains triphenylpararosaniline, commercial triphenylpararosaniline-blue gives no trace of the picrate.

Diphenylaminofuchsonephenylimonium benzoate is formed when tri-*p*-anisylcarbinol is heated with aniline and benzoic acid. It crystallises in small, blue, transparent leaflets, and, when shaken with aqueous sodium hydroxide, yields diphenylaminofuchsonephenylimine,

$$C(C_6H_4\cdot NHPh)_2{:}C_6H_4{:}NPh,$$

which crystallises in plates and melts at 237—238°. It combines readily with aniline in pyridine, or with methyl alcohol, more slowly with ethyl alcohol or methylaniline; the alkyl ethers and anilides so formed are obtained as syrups. The colour-base is reduced to the leucobase; with acids it forms the salts of triphenylpararosaniline (diphenylaminofuchsonephenylimonium salts). The *chloride* crystallises in stellate clusters of needles; the picrate mentioned above crystallises in glistening, bronze leaflets. The action of water on the colour-base in presence of a trace of an acid leads to the formation of the carbinol (triphenylpararosaniline), which crystallises with benzene of crystallisation and melts at 85°. *Triphenylparaleucaniline* crystallises in glistening needles and melts at 182—184°.

The action of sodium methoxide on pararosaniline in methyl-alcoholic solution leads to the formation of the *methyl ether* of triaminotriphenylcarbinol (Fischer, Abstr., 1901, i, 82). It crystallises in rhombic leaflets containing 1 mol. of ether of crystallisation, sinters, and loses ether at 105°. At 110°, the ether commences to decompose with the loss of methyl alcohol.

The *methyl ether* of triaminotritolylcarbinol crystallises in long leaflets and melts and decomposes at 178°. The *methyl ether* of hexamethyltriaminotriphenylcarbinol is formed by the action of sodium

methoxide on crystal-violet. It crystallises in rhombic plates and melts at 159—160° when heated in a closed capillary.

Whilst the monoaminotriphenylcarbinols do not crystallise, but form stable crystalline carbinol salts, the di- and tri-amino-compounds are crystalline, and form unstable carbinol salts (not yet isolated), but stable crystalline fuchsoneimonium salts.

Fuchsoneimine has not been isolated, as, on formation, it immediately polymerises, or, in presence of water, forms the carbinol. In benzene solution, monoaminofuchsoneimine polymerises slowly, the diamino-compound still more so; the increase of the amino-groups is accompanied by increase in the stability of the dye salts and of their usefulness as dyes. G. Y.

Chloralamino-compounds. I. S. GÄRTNER (*Annalen*, 1904, 332, 226—245).—The interaction of trichloroethylideneanthranilic acid with phenylhydrazine and semicarbazide has been studied, the reaction with the former substance being represented thus:

$$NH_2\cdot NHPh + CCl_3\cdot CH{:}N\cdot C_6H_4\cdot CO_2H \longrightarrow$$
$$NHPh\cdot N{:}CCl\cdot CH{:}N\cdot C_6H_4\cdot CO_2H + H_2O \rightarrow$$
either $NHPh\cdot N{:}C(OH)\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$ or
$$NHPh\cdot NH\cdot CO\cdot CH{:}N\cdot C_6H_4\cdot CO_2H.$$

Semicarbazide reacts in a similar manner.

The *monophenylhydrazide* of *2-carboxyphenyliminoacetic acid* separates from a solution of trichloroethylideneanthranilic acid in alcohol, to which an aqueous solution of phenylhydrazine sulphate has been added, and forms pale yellow prisms melting and decomposing at 243°; it is soluble in the equivalent quantity of a solution of sodium carbonate or sodium hydroxide, with an intense yellow coloration; on addition of excess of alkali, the salt separates; the *potassium* salt, $C_{15}H_{12}O_3N_3K$, crystallises in yellow needles, the *calcium* salt in needles with $8\frac{1}{2}H_2O$; the *barium* salt is anhydrous. The compound is only hydrolysed after prolonged boiling with a large excess of alkali hydroxide. The *ethyl* ester, prepared from the silver salt and ethyl iodide, crystallises in white needles or yellow prisms melting at 140—141°, and the *acetyl* compound in needles melting at 268°. When the acetyl derivative is heated under reduced pressure, the *anhydride*, $C_6H_4{<}{\begin{matrix} N{:}CH\cdot CO \\ CO\text{——}N\cdot NPhAc \end{matrix}}$, is obtained as yellow needles melting at 260—262°, and is decomposed when heated under the ordinary pressure, yielding acetanilide. If the anhydride is warmed with dilute sodium hydroxide, the acetyl group is removed, water added, and the original phenylhydrazide regenerated, together with a neutral *compound* which melts at 170° and gives a green coloration with sulphuric acid.

When oxidised with dilute nitric acid, the phenylhydrazide yields *p*-nitrosalicylic acid, oxalic acid, and traces of benzoic acid. If permanganate is used instead of nitric acid, oxalylanthranilic acid is produced (melting and decomposing at 210°); the *silver* salt was analysed.

The *semicarbazide* of *2-carboxyphenyliminoacetic acid*,
$$NH_2\cdot CO\cdot N_2H_4\cdot CO\cdot CH{:}N\cdot C_6H_4\cdot CO_2H,$$

prepared from semicarbazide hydrochloride and trichloroethylidene-anthranilic acid, crystallises in needles decomposing at 278—280°; the *calcium* salt (with $11H_2O$) and the barium salt (with $9\frac{1}{2}H_2O$) crystallise in long needles. K. J. P. O.

Azo-dyes from 3 : 3'-Dihydroxy-2 : 2'-dinaphthyl. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1904, 138, 1618—1619).—*3 : 3'-Dihydroxy-2 : 2'-dinaphthyl-1 : 1'-disazo-β-naphthalene*, $C_{20}H_{10}(OH)_2(N_2 \cdot C_{10}H_7)_2$, obtained by the action of 2 mols. of diazotised β-naphthylamine on 1 mol. of 3 : 3'-dihydroxy-2 : 2'-dinaphthyl, has a bright red colour, is insoluble in water, soluble in alcohol forming a bright carmine-red solution, and soluble in sulphuric acid with a blue colour. *3 : 3'-Dihydroxy-2 : 2'-dinaphthyl-1-azo-β-naphthalene*, $C_{20}H_{13}O_2 \cdot N_2 \cdot C_{10}H_7$, prepared from 1 mol. of diazotised β-naphthylamine and 1 mol. of 3 : 3'-dihydroxy-2 : 2'-dinaphthyl, has a violet colour, is insoluble in water, forms a violet solution in sulphuric acid, and its sulphonic derivative is soluble in water and dyes wool a reddish-brown. *3 : 3'-Dihydroxy-2 : 2'-dinaphthyl-1-azo-p-nitrobenzene*,

$$C_{20}H_{13}O_2 \cdot N_2 \cdot C_6H_4 \cdot NO_2,$$

has a red colour, is very slightly soluble in water, and forms a brown solution in sulphuric acid. *3 : 3'-Dihydroxy-2 : 2'-dinaphthyl-1 : 1'-disazo-p-nitrobenzene* has an orange colour, is very slightly soluble in water, but the solution colours wool a bright orange; it forms a brown solution in sulphuric acid. *3 : 3'-Dihydroxy-2 : 2'-dinaphthyl-1 : 1'-disazodiphenyl*, $\begin{array}{l} OH \cdot C_{10}H_5 \cdot N_2 \cdot C_6H_4 \\ \quad | \qquad\qquad\quad | \\ OH \cdot C_{10}H_5 \cdot N_2 \cdot C_6H_4 \end{array}$, has a brown colour, is insoluble in water, and forms a greyish-green solution in sulphuric acid. *3 : 3'-Dihydroxy-2 : 2'-dinaphthyl-1-azoanisole* is brown, insoluble in water, and soluble in nitric acid. The existence of azo-derivatives of β-dinaphthol points to the linking of the two naphthalene rings being in the 2 : 2'- and not the 1 : 1'-position, as hitherto assumed. M. A. W.

Reactions of αβ-Diketobutyric Esters. I. Action of Phenylhydrazine. LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1904, 139, 134—136. Compare this vol., i, 556).—Ethyl diketobutyrate-phenylhydrazone is probably the β-derivative,

$$NHPh \cdot N{:}CMe \cdot CO \cdot CO_2Et,$$

for it reacts with *p*-nitrophenylhydrazine to form 4-*p*-nitrobenzeneazo-1-phenyl-3-methyl-5-pyrazolone identical with the compound prepared by Bülow by the action of phenylhydrazine on ethyl *p*-nitrobenzene-azoacetoacetate (compare Abstr., 1899, i, 271), in which the phenylhydrazone grouping is in the β-position; the following equation therefore represents the reaction:

$$\begin{array}{l} CMe \cdot CO \cdot CO_2Et \\ \| \\ N \cdot NHPh \end{array} + NH_2 \cdot NH \cdot C_6H_4 \cdot NO_2 =$$

$$NPh{<}\begin{array}{l} N = CMe \\ \quad\quad\ | \\ CO \cdot C{:}N \cdot NH \cdot C_6H_4 \cdot NO_2 \end{array} + C_2H_6O + H_2O.$$

Further, on boiling an acetic acid solution of the ethyldiketobutyratephenylhydrazone, it is converted into rubazonic acid,

$$NPh<\begin{matrix}CO\cdot CH\cdot N:CH\cdot CO \\ N{=\!=}CMe \quad CMe:N\end{matrix}>NPh$$

(compare Knorr, Abstr., 1887, 602).

By the action of phenylhydrazine on ethyl diketobutyrate at a high temperature, 1-phenyl-3-methyl-5-pyrazolone-4-phenylhydrazone,

$$NPh<\begin{matrix}N{=\!=}CMe \\ CO\cdot C:N\cdot NHPh\end{matrix},$$

is obtained, identical with the compound obtained by Knorr, (1) by the action of diazobenzene chloride on phenylmethylpyrazolone (compare Abstr., 1887, 602); (2) by boiling rubazonic acid and phenylhydrazine in acetic acid solution (compare Abstr., 1888, 724); and by Japp and Klingemann by the action of phenylhydrazine on ethyl phenylhydrazoneacetoglyoxylate (compare Trans., 1888, 53, 530).

M. A. W.

Compounds of Albumin with Bismuth and Formaldehyde. Kalle & Co. (D.R.-P. 150201).—Bismuthose, prepared by adding egg-albumin to a solution of bismuth nitrate and sodium chloride (compare D.R.-P. 117269), swells to a gelatinous mass with water. This property is destroyed when formaldehyde is added. The product is washed until neutral, pressed, and dried. Hot dilute acids or alkalis hydrolyse it, setting free formaldehyde.

C. H. D.

Combinations of Mucoids with other Proteids. E. R. Posner and William J. Gies (*Amer. J. Physiol.*, 1904, **11**, 404—436).—Addition of a solution of a mucoid to that of another proteid causes the formation of a precipitate, which is stated to be a compound and not a mixture of the mucoid and proteid. The glucothionic acid in mucoid is believed to be concerned in the reaction.

W. D. H.

The Carbohydrate Group in Proteids. Leo Langstein (*Zeit. physiol. Chem.*, 1904, **42**, 171—174).—Polemical. The results recorded by Abderhalden, Bergell, and Dorpinghaus (this vol., i, 640) are not new, but merely confirmatory of work previously published by others, including the author.

W. D. H.

Carbohydrates from Serum Globulins. II. Leo Langstein (*Monatsh.*, 1904, **25**, 453—463. Compare Abstr., 1902, i, 66; 1903, i, 374, 734).—When boiled with water (Mörner, Abstr., 1894, i, 352), with dilute alkali hydroxides, or with baryta solution, serum globulin yields a polysaccharide, which contains nitrogen and resembles Fränkel's albumin (Abstr., 1899, i, 396), but does not give Ehrlich's reaction with dimethylaminobenzaldehyde. When boiled with 2·2 per cent. hydrochloric acid, it yields glucosamine. The dextrose of globulin is not a component of the albumin molecule, but is probably in molecular combination, the stability being equal to that of the water of crystallisation of salts.

G. Y.

The Amount of Sulphur in the Digestion Products of Casein. Waclaw von Moraczewski (*Beitr. chem. Physiol. Path.*, 1904, **5**, 489—499).—The amount of sulphur in paranuclein is constant, and

independent of the time of the digestion with pepsin-hydrochloric acid. During digestion, a part of the sulphur of the casein is lost, and this amount increases with the intensity of the digestive process.

W. D. H.

Nucleic Acid. Carl Luca Alsberg (*Chem. Centr.*, 1904, ii, 133—134; from *Arch. exp. Path. Pharm.*, 51, 239—247).—Nucleic acid, prepared from the semen of the turbot, *Lota vulgaris*, is identical with the acid obtained from salmon milt. By digesting copper nucleate with a 2 per cent. solution of sulphuric acid for 8—10 days at 38—40°, 1 mol. of purine base is eliminated and *heminucleic acid*,

$$C_{35}H_{51}O_{15}N_9,2P_2O_5,3H_2O,$$

is obtained. This acid is distinguished from nucleic acid by the fact that solutions of its alkali salts in dilute acetic acid are not precipitated by hydrochloric acid or cupric chloride. Experiments on the action of acids on nucleic acid confirmed Schmiedeberg's results (Abstr., 1900, i, 267); the acid loses a portion of the purine bases with ease, but the rest only with difficulty, whilst the nucleotin is uniformly decomposed. The barium compound of a substance $C_{47}H_{81}O_{30}N_9,2P_2O_5$, prepared by boiling copper nucleate for 24 hours with a saturated solution of baryta water, was found to consist of a mixture of heminucleic acid and a compound $C_{12}H_{30}O_{15}$. A small quantity of the barium salt of nucleotin, $Ba_4C_{30}H_{34}O_{13}N_4,11H_2O$, has been obtained by heating copper nucleate with baryta water in superheated steam.

E. W. W.

Epinephrine (Adrenaline). Emil Abderhalden and Peter Bergell (*Ber.*, 1904, 37, 2022—2024).—Epinephrine is very liable to oxidation during the course of separation and purification. By purifying in an atmosphere of hydrogen, a substance was obtained which gave analytical values corresponding with the formula $C_9H_{13}O_3N$ suggested by Pauly. Abel's formula, $C_{10}H_{13}O_3N,\frac{1}{2}H_2O$, appears to have been based on the analysis of a partially-oxidised product containing a low percentage of carbon and hydrogen. T. M. L.

Products of Distillation of Hæmatin with Zinc Dust. J. A. Milroy (*Proc. Physiol. Soc.*, 1904, xxiv—xxvi; *J. Physiol.*, 31).—At least three volatile substances are obtained by the distillation of hæmatin with zinc dust, two resembling in their spectroscopic appearances hæmatoporphyrin and urobilin, although differing from the latter in regard to solubility, and one probably allied to the hæmopyrrole obtained by Nencki and Zaleski. W. D. H.

β-Hæmin. Karl A. H. Mörner (*Zeit. physiol. Chem.*, 1904, 41, 542—547).—The author agrees with Küster's conclusion (this vol., i, 357) that there is only one hæmin, and that β-hæmin, acetohæmin, and hæmin are identical. It is suggested that β-hæmin may contain a small amount of an ethereal derivative of hæmin. J. J. S.

Function of Peroxides in the Living Cell. IX. Rate of the Peroxydase Reaction. Alexis Bach and Robert Chodat (*Ber.*, 1904, 37, 2434—2440. Compare this vol., i, 542).—It had previously been shown that, during the oxidation of pyrogallol, the peroxydase used and hydrogen peroxide react in definite proportions. The rate of the action of the peroxydase on hydrogen peroxide has now been measured, the amount of oxygen liberated being measured by its action on hydriodic acid. The rate at which the peroxydase disappears increases with the concentration of the peroxydase, but more quickly than the latter concentration increases. In the reaction between hydriodic acid and hydrogen peroxide in the presence of the peroxydase, the latter possesses a much greater power of rendering the hydrogen peroxide active than it does during the oxidation of pyrogallol.

The rate of the peroxydase reaction follows the Law of Mass Action, when the reaction is not destroyed by the presence of by-products.

The peroxydase is considered to be a ferment, although it gradually disappears during the oxidation. A. McK.

Inhibitory Influence of Foreign Molecules on the Action of Histozymes, and Ferments on Amides and Glucosides. Max Gonnermann (*Pflüger's Archiv*, 1904, 103, 225—256. Compare Abstr., 1903, i, 590).—The action of emulsin on glucosides and of extracts of animal organs on amides and glucosides was investigated in the presence of inhibitory agents such as ammonium sulphate, potassium chloride, quinine, &c. Differences in the amount and rate of inhibition are noted. W. D. H.

Conversion of Nitrobenzene into Aniline by means of Philothion and Yeast Reductases. M. Emmanuel Pozzi-Escot (*Chem. Centr.*, 1904, i, 1646—1647; from *Bull. Assoc. Chem. Sucr. Dist.*, 21, 1073—1075. Compare Abstr., 1903, i, 670, and Abelous and Gérard Abstr., 1900, ii, 226).—The following experiment shows that nitrobenzene may be reduced to aniline by the action of philothion on reducing diastases. Beer or wine yeast which has been pressed, but not dried, is mixed with alcohol and water, and after remaining 30—40 hours the mixture is filtered and a few drops of nitrobenzene added to the filtrate. The odour of nitrobenzene disappears in 24 hours. The presence of aniline cannot be detected directly, however, by the ordinary methods, but after neutralising with hydrochloric acid and removing the alcohol by distillation the characteristic reactions of the base are readily obtained. E. W. W.

Organic Chemistry.

Sodium Derivatives of Acetylene. M. Skosarewsky (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 863—872).—The sodium derivatives of acetylene were first prepared by Berthelot (*Ann. Chim. Phys.*, 1866, [iv], 9, 385), who ascribed to them the formulæ C_2Na_2 and C_2HNa. Later, however, Moissan (Abstr., 1898, ii, 332, and 1899, i, 241) suggested that the mono-sodium derivative of acetylene is more accurately represented by the formula C_2Na_2,C_2H_2. The results of the author's experiments show, on the other hand, that all the known facts concerning this compound are explained by the composition CH⋮CNa, and that the sodium derivatives of mono-substituted acetylenes are represented by CR⋮CNa.

The action of iodine on the mono-sodium derivative of acetylene gives rise to the compound C_2HI_3 in the following manner: (1) CH⋮CNa + I_2 = CH⋮CI + NaI, and (2) CH⋮CI + I_2 = CHI⁚CI_2. If the formula of the sodium derivative were C_2Na_2,C_2H_2, the action of iodine should yield $C_2H_2I_4$.

Further, when heated in an atmosphere of carbon dioxide, this sodium derivative yields exclusively the compound CH⋮C·CO_2Na, and not CO_2Na·C⋮C·CO_2Na or CNa⋮C·CO_2Na, as should be the case if the formula C_2Na_2,C_2H_2 were the correct one. T. H. P.

Action of Nitrogen Peroxide on Diallyl. K. W. Sidorenko (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 898—905).—On passing nitrogen peroxide (approx. $2NO_2$) into an ethereal solution of diallyl (1 mol.) kept cool by snow and salt, and reducing the product obtained by means of tin and hydrochloric acid, an unsaturated *amine*, $C_6H_{10}(NH_2)_2$, is obtained, the *platinichloride*, *hydrochloride*, and *oxalate* of which were prepared and analysed; the last-named salt melts and decomposes at 166° if slowly heated, and at about 190° if rapidly heated. The structure of the amine is probably

CH_2⁚CH·CH_2·CH_2·CH(NH_2)·CH_2·NH_2. T. H. P.

Slow Oxidation of Cyanogen and of Cyanides by Free Oxygen. Marcellin Berthelot (*Compt. rend.*, 1904, **139**, 169—177). —The author has investigated the action of oxygen on aqueous and alcoholic solutions of potassium cyanide, hydrogen cyanide, and cyanogen, the influence of light on the change being also examined. The solutions were in most cases in contact with mercury, and at the end of the experiment were examined for the presence of the metal.

Aqueous or alcoholic potassium cyanide slowly absorbs oxygen; the rate of absorption increases with rise of temperature, and is greater in sunlight than in the dark. In presence of mercury, the metal dissolves, especially when the system is insolated. An aqueous solution of hydrocyanic acid also absorbs oxygen, although to a much smaller extent.

Aqueous or alcoholic solutions of cyanogen take up oxygen, and the cyanogen soon disappears, carbon dioxide being produced, and in presence of mercury traces of the metal are dissolved, the action being accelerated by light.

Further experiments with aqueous cyanogen solutions containing potassium cyanide or hydrogen cyanide gave similar results. In the case of an alcoholic solution containing cyanogen and potassium cyanide, the absorption of oxygen, whether in sunlight or in the dark, is not accompanied by solution of mercury.

A solution of potassium hydroxide in absolute alcohol also absorbs oxygen in sunlight, but mercury is not dissolved. H. M. D.

Changes in the Composition of some Ferrocyanides of Cadmium and Zinc after Precipitation. EDMUND H. MILLER and M. J. FALK (*J. Amer. Chem. Soc.*, 1904, 26, 952—959. Compare Abstr., 1902, i, 429).—On adding a slight excess of potassium ferrocyanide to a dilute solution of cadmium chloride containing ammonium chloride at 50—100°, a crystalline precipitate having the composition $Cd(NH_4)_2Fe(CN)_6$ is obtained (compare Waring, this vol., ii, 211); when, however, the cadmium chloride is added to an excess of potassium ferrocyanide either at 50° or at 100°, a mixture having the composition $3CdK_2Fe(CN)_6,7Cd(NH_4)_2Fe(CN)_6$ is precipitated.

When cadmium potassium ferrocyanide, $CdK_2Fe(CN)_6$, is agitated with dilute ammonia at 50° for a week, it is transformed into a mixture of $6Cd_2Fe(CN)_6,3Cd(NH_4)_2Fe(CN)_6$ and $CdK_2Fe(CN)_6$; with ammonium chloride under similar conditions, a larger proportion of normal cadmium ferrocyanide is formed, the product having the composition $3Cd_2Fe(CN)_6,6Cd(NH_4)_2Fe(CN)_6,CdK_2Fe(CN)_6$.

Cadmium ammonium ferrocyanide, $Cd(NH_4)_2Fe(CN)_6$, is similarly transformed by dilute aqueous potassium hydroxide into a mixture having the same composition as that formed when cadmium chloride is precipitated with an excess of potassium ferrocyanide, namely, $3CdK_2Fe(CN)_6,7Cd(NH_4)_2Fe(CN)_6$. Application is made of these facts to the theory of the cadmium precipitation.

The precipitate obtained by adding potassium ferrocyanide to a solution of zinc chloride containing ammonium chloride at 60° has the composition $Zn_{15}(NH_4)_8K_2[Fe(CN)_6]_{10}$. This complex salt is transformed by agitation with potassium chloride at 70° into the simpler mixture $Zn_2Fe(CN)_6,K_2Fe(CN)_6$, the ferrocyanide obtained in the precipitation of zinc when no ammonium chloride is present; conversely, the latter mixture is transformed into the former by agitation with ammonium chloride. The bearing of these facts on the titration of zinc by potassium ferrocyanide is discussed. W. A. D.

Preparation of Trichloro*iso*propyl Alcohol. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 151545).—Trichloro*iso*propyl alcohol, $CCl_3·CHMe·OH$ (Thurnlackh, Abstr., 1882, 295), may be prepared by adding magnesium methyl iodide or magnesium methyl bromide to a cooled solution of chloral in dry ether, acidifying and distilling. It melts at 49·2° and has hypnotic properties (compare this vol., i, 279). C. H. D.

Oxoctenol. N. Prileschaeff (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 872—881).—The reduction of oxoctenol in ethyl-alcoholic solution by means of sodium yields a *glycol*, $C_8H_{18}O_2$, which crystallises from light petroleum in well-formed prisms, melts at 64·5—65°, is very volatile, and has a pleasant camphoraceous odour. On oxidation with 1 per cent. potassium permanganate solution, it gives oxoctenol. No intermediate compound resembling this glycol or giving oxoctenol on oxidation could be found among the products obtained by oxidising *iso*butylene, which is the method of preparing oxoctenol (Butleroff, Abstr., 1882, 936).

Oxoctenol does not react with hydroxylamine, hydrazine hydrate, semicarbazide, *p*-bromophenylhydrazine, or phenylhydrazine. When dehydrated by distilling with anhydrous oxalic acid, it yields an unsaturated *ketone*, $C_8H_{14}O$, which boils at 137—139° under 754 mm. pressure, readily decolorises permanganate solution and absorbs bromine (2 atoms), and gives a *carbazone*, $C_9H_{18}ON_3$,, melting at 151·5—152·5°. The products of the oxidation of this ketone by permanganate are acetic, trimethylacetic, and formic acids. These results would indicate a hydroxy-ketonic structure for oxoctenol, but as the above dehydration takes place in a strongly acid liquid, it is probable that isomeric change takes place, inasmuch as oxoctenol does not react with the ordinary reagents for the carbonyl group.

Besides the glycol referred to above, the products of the reduction of oxoctenol by sodium ethoxide comprise also a *hydroxy-ketone*, $CMe_3·CO·CMe_2·OH$, which is isomeric with oxoctenol and yields a *semicarbazone*, $C_9H_{19}O_2N_3$, crystallising from alcohol in feathery, drusy masses, melting at 185·5—186·5°. This action of alkalis on oxoctenol must be regarded, not as an isomeric change, but as simultaneous reduction and oxidation, similar to the action of alkalis on aldehydes.

The above facts show clearly that oxoctenol is not to be regarded as the first product of the oxidation of an oxide previously formed from *iso*butylene, as was suggested by Butleroff (*loc. cit.*). T. H. P.

Preparation of Acetyl Chloride. Alfred Wohl (D.R.-P. 151864).—The reaction between calcium acetate and sulphuryl chloride is generally very incomplete, but may be rendered almost complete by prolonged mixing of the reacting compounds in a ball mill. A double compound is first formed from the sulphuryl chloride and a part of the calcium acetate, which gives up no acetyl chloride to benzene or on heating, and decomposition into acetyl chloride and calcium sulphate only occurs after prolonged mechanical mixing. C. H. D.

Preparation of Nitroacetic Esters. Louis Bouveault and André Wahl (*Bull. Soc. chim.*, 1904, [iii], 31, 847—854).—The methods previously described by Franchimont (Abstr., 1889, 1143) and the authors (Abstr., 1901, i, 5 and 445) for the preparation of these esters do not give satisfactory yields. The following process is now recommended: ethyl acetoacetate (50 grams) is dissolved in acetic anhydride (25 grams) and the liquid, previously warmed to 35°, is thoroughly agitated by means of a current of air, while a mixture of

anhydrous nitric acid (27 grams) with cold acetic anhydride (27 grams) is added, drop by drop, from a bromine tube dipping into the liquid, the temperature being maintained at 32—34°. The mixture is then thrown into water, and from the precipitated oil, which also contains ethyl bisanhydronitroacetate and dinitroacetate (Bouveault and Bongert, Abstr., 1901, i, 579), ethyl nitroacetate is isolated by solution in ether and extraction with an aqueous solution of sodium hydroxide.

Methyl nitroacetate, similarly prepared, boils at 94—95° under 16 mm. pressure and is slightly soluble in water (compare Wieland, Abstr., 1903, i, 769). iso*Butyl nitroacetate* is a colourless liquid, which distils at 102° under 8 mm. pressure and furnishes a colourless, crystalline *potassium* salt. With this ester is produced a small quantity of *iso*butyl diketobutyrate (this vol., i, 557). T. A. H.

Dissimilarity in the Reactions of *d*- and *l*-Lactic Acids. ÉMILE JUNGFLEISCH (*Compt. rend.*, 1904, **139**, 203—206).—Solutions of quinine *d*-lactate or quinine *l*-lactate were precipitated with the hydroxide of barium, calcium, or potassium, the quinine removed by ether or amyl alcohol, and the rotatory power of the metallic lactate in solution, as well as that of the zinc lactate obtained by double decomposition, was measured. The rotatory power of the solution obtained from the *d*-lactate differed in every case from that of the solution obtained from the *l*-lactate. Using calcium hydroxide to precipitate the quinine, the solutions from the *d*- and *l*-lactates gave respectively for $\alpha_D - 1{\cdot}5°$ and $+0{\cdot}5°$. These facts indicate that the *d*- and *l*-lactic acids differ considerably in their behaviour; both undergo racemisation, but the *l*-acid is more readily transformed (compare this vol., i, 645).

H. M. D.

Pyruvic Acid as a Decomposition Product of Proteids. KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1904, **42**, 121—131. Compare Suter, Abstr., 1895, i, 691).—Horn, human hair, and blood serum all yield small amounts of pyruvic acid when heated at 90° with dilute hydrochloric acid. The acid was characterised by conversion into its phenylhydrazone, which melts at 180—182°. Casein yields a mixture of acids which with phenylhydrazine gives a mixture of phenylhydrazones melting at about 150° and probably derived from pyruvic acid and the homologous propionylformic acid.

It is not probable that pyruvic acid stands in any simple relationship to cystin. J. J. S.

Vinyldimethylacetic Acid. EDMOND E. BLAISE and A. COURTOT (*Compt. rend.*, 1904, **139**, 292—294).—The acid obtained by boiling an aqueous solution of sodium β-iodo-αα-dimethylglutarate (compare Abstr., 1903, i, 604) or by distilling αα-dimethylglutaconic acid (compare Perkin, Trans., 1902, **81**, 256) is not dimethylvinylacetic acid, as stated by Perkin, but the isomeric pyroterebic acid, with which it has been identified by means of its boiling point, its anilide, its calcium salt, and its conversion into *iso*caprolactone by the action of sulphuric acid (compare Blanc, this vol., i, 647). The formation of pyroterebic acid from αα-dimethylglutaconic acid involves therefore the elimination of carbon dioxide from the carboxyl group in the α-position

and the migration of the ethylenic linking from the $\beta\gamma$- to the $\alpha\beta$-position, thus:

$CO_2H\cdot CMe_2\cdot CH{:}CH\cdot CO_2H \longrightarrow$
$[CHMe_2\cdot CH{:}CH\cdot CO_2H] \longrightarrow CMe_2{:}CH\cdot CH_2\cdot CO_2H.$

Bouveault's $\alpha\alpha$-dimethyl*iso*crotonic acid (compare Abstr., 1900, i, 131) is identical with dimethylvinylacetic acid, since it yields dimethylmalonic acid on oxidation with potassium permanganate. It crystallises at a low temperature and does not yield a lactone on treatment with sulphuric acid. M. A. W.

Action of Potassium Nitrite on Ethyl Mucobromate. HENRY B. HILL and OTIS F. BLACK (*Amer. Chem. J.*, 1904, 32, 228—242).—Ethyl mucobromate, $CHO\cdot CBr{:}CBr\cdot CO_2Et$, reacts with potassium nitrite in dilute alcoholic solution, forming *potassium ethyl nitromaleate*, $CO_2Et\cdot C(NO_2){:}CH\cdot CO_2K$, crystallising in colourless prisms. The *methyl* ester, from methyl mucobromate, is similar. Both esters are oxidised by bromine and water to dibromonitromethane and glyoxylic acid. Ammonia forms a mixture of the potassium and ammonium salts of *nitromaleamic acid*, $NH_2\cdot CO\cdot C(NO_2){:}CH\cdot CO_2H$, which decomposes on evaporation, but forms stable *potassium*, *ammonium*, and *silver* salts. Barium hydroxide reacts with potassium ethyl nitromaleate to form a basic barium nitromalate, which is decomposed by hydrochloric acid, forming *β-nitrolactic acid* (*β-nitro-α-hydroxypropionic acid*), $NO_2\cdot CH_2\cdot CH(OH)\cdot CO_2H$, which crystallises from ether or chloroform in small, white prisms and melts at 76—77° (uncorr.). It dissolves readily in water, alcohol, or ether, more sparingly in chloroform. By crystallising its strychnine salt and decomposing with hydrochloric acid, a lævorotatory modification is obtained. The *barium*, *calcium*, and *silver* salts are described. The *acetyl* derivative crystallises from ether and chloroform in large, white octahedra, melts at 90—91°, and dissolves readily in water. Tin and hydrochloric acid reduce nitrolactic acid to *iso*serin (β-amino-α-hydroxypropionic acid). C. H. D.

***iso*Erucic Acid.** GIACOMO PONZIO (*Gazzetta*, 1904, 34, ii, 50—55).—By adding hydrogen iodide to erucic acid and afterwards removing it by means of alcoholic potassium hydroxide, Alexandroff and Saytzeff (Abstr., 1893, i, 549) obtained an acid melting at 54—56° to which they gave the name *iso*erucic acid and the constitution

$$CH_3\cdot[CH_2]_{18}\cdot CH{:}CH\cdot CO_2H.$$

The authors have prepared this acid and studied its transformations, from which they find that it has the same structure as erucic acid, namely, $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_{11}\cdot CO_2H$, so that Alexandroff and Saytzeff's statement (*loc. cit.*) that these two acids are structural isomerides is inaccurate.

The action of bromine in acetic acid solution on *iso*erucic acid yields dibromobehenic acid, which, when treated with alcoholic potassium hydroxide at 130—140° gives behenolic acid,

$$CH_3\cdot[CH_2]_7\cdot C{:}C\cdot[CH_2]_{11}\cdot CO_2H.$$

When heated with nitric acid of sp. gr. 1·4, *iso*erucic acid is transformed into nonylic and brassilic acids together with a small quantity of dinitrononane. T. H. P.

Resolution of Racemic Acid by means of Aspergillus Niger. SEBASTIANO CONDELLI (*Gazzetta*, 1904, 34, ii, 86—96. Compare Ulpiani and Condelli, Abstr., 1900, ii, 493).—The optimum temperature for the decomposition of racemic acid by *Aspergillus niger* is about 35°. Both the isomerides undergo further decomposition, the *d*-tartaric acid formed being destroyed more at low temperatures, and the *l*-acid at the higher temperatures. Probably the *l*-acid becomes transformed into the *d*-form, which is readily attacked. T. H. P.

Action of some Fatty Acids on Starch. A. G. KLDIASCHWILI (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 905—908).—The direct action of formic acid on starch yields the monoformyl derivative of this carbohydrate, to which, on the basis of cryoscopic measurements in chloroacetic acid and phenol, the formula $(C_7H_{10}O_6)_6$ or $(C_7H_{10}O_6)_6,H_2O$ is ascribed. The author is not convinced of the chemical individuality of the compound owing to the possibility of the presence of the corresponding ethers of various dextrins, but it is shown that the ether of ordinary dextrin is not present. Analogous compounds are obtained by the action of mono-, di-, and tri-chloroacetic acids on starch. The mono- and di-chloro-compounds dissolve readily in acetone, and have been obtained pure. The amount of acid in these ethers shows them to be mono-acyl compounds. With iodine, these compounds give no characteristic coloration, but, after hydrolysis with potassium hydroxide, the monochloro-derivative gives a dextrin coloration with iodine, whilst the dichloro-compound yields no coloration, and the trichloro-ether only an indefinite one. T. H. P.

Theory of the Process of Saponification. LUIGI BALBIANO (*Gazzetta*, 1904, 34, ii, 55—56).—The author replies to the criticisms of Lewkowitsch (Abstr., this vol., i, 6 and 283. Compare Balbiano, Abstr., 1903, i, 547). T. H. P.

Propanetrisulphonic Acid. WILLIAM B. SCHOBER (*Amer. Chem. J.*, 1904, 32, 165—167).—The only derivatives of propanetrisulphonic acid hitherto described are the barium salts prepared by Schaüfelin (*Annalen*, 1868, 148, 117).

When $\alpha\beta\gamma$-tribromopropane (tribromohydrin) is heated with ammonium sulphite, *ammonium propanetrisulphonate*,

$$C_3H_5(SO_3 \cdot NH_4)_3,H_2O,$$

is obtained. The barium salt crystallises with $5H_2O$. E. G.

Reactions of the Hexoses. RUDOLF OFNER (*Monatsh.*, 1904, 25, 611—620).—Seliwanoff's reaction (Abstr., 1887, 459) takes place with aldoses as well as ketoses, if the concentration of the hydrochloric acid is favourable. If used as a reaction for ketoses, the hydrochloric acid must not be stronger than 12 per cent. Contrary to Neuberg's statement (Abstr., 1902, i, 264), osazones are formed by the interaction of secondary asymmetric hydrazines and aldoses. The action of *as*-phenylbenzylhydrazine on dextrose or its phenylbenzylhydrazone leads to the formation of an osazone identical with Neuberg's lævulose-phenylbenzylosazone.

When dextrosephenylbenzylhydrazone is boiled with phenylhydrazine hydrochloride and sodium acetate in dilute alcoholic solution, the product is phenylglucosazone. G. Y.

Decomposition of Nitrocellulose at Temperatures below that of Ignition. A. V. SAPOSCHNIKOFF and M. BORISOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 836—841).—Nitrocellulose decomposes, not only on ignition, but also at temperatures not sufficiently high to ignite it. On heating a mixture of nitrocellulose containing 13·25 per cent. of nitrogen with quartz sand in an electric thermostat at 150° ± 1°, it loses 41·3 per cent. of its weight and decomposes according to the equation: $C_{24}H_{29\cdot31}(NO_3)_{10\cdot7}O_{9\cdot31} = C_{20\cdot14}H_{8\cdot27}O_{22\cdot55}N_4 + 2\cdot58NO + 1\cdot88CO_2 + 1\cdot981CO + 2\cdot06N_2 + 10\cdot52H_2O$. With nitrocellulose containing 12 per cent. of nitrogen, the loss in weight is 43·2 per cent. and the equation expressing the decomposition: $C_{24}H_{30\cdot72}(NO_3)_{9\cdot28}O_{10\cdot72} = C_{20\cdot82}H_{4\cdot8}O_{19\cdot5}N_{2\cdot76} + 1\cdot52NO + 1\cdot42CO_2 + 1\cdot764CO + 2\cdot50N_2 + 12\cdot96H_2O$.

On comparing these results with the following equations, representing the changes on igniting the nitrocellulose: (1) $C_{24}H_{29}(NO_3)_{11}O_9 = 12CO_2 + 12CO + 8\cdot5H_2 + 5\cdot5N_2 + 6H_2O$ and (2) $C_{24}H_{31}(NO_3)_9O_{11} = 6\cdot84CO_2 + 16\cdot51CO + 0\cdot643CH_4 + 7\cdot39H_2 + 4\cdot5N_2 + 4\cdot92H_2O$, it will be seen that the slow combustion occurring at the lower temperatures differs from the ignition in yielding a solid nitrogenous residue, in giving nitric oxide (and, at the beginning of the reaction, nitrogen peroxide), and in yielding no hydrogen but an increased proportion of water. When heated at 150° without sand, the nitrocelluloses decompose more rapidly and completely. Thus, the one containing 13·25 per cent. of nitrogen loses 91·1 per cent. of its weight; 63·2 per cent. of this loss is water and the rest a gaseous mixture having the percentage composition: NO, 27·74; CO_2, 25·10; CO, 17·44; N_2, 29·72.

At 135°, gaseous mixtures were obtained from the two nitrocelluloses having the percentage compositions by volume:

	Nitrocellulose with 13·25 per cent. N.	Nitrocellulose with 12 per cent. N.
NO	34·52	28·33
CO_2	29·38	21·33
CO	13·43	19·67
N_2	22·67	30·67

T. H. P.

Cellose. LÉON MAQUENNE and W. GOODWIN (*Bull. Soc. chim.*, 1904, [iii], 31, 854—859. Compare Skraup and collaborators, Abstr., 1899, i, 852, and 1901, i, 370).—Cellose, prepared from cellulose by a modification of Skraup's process (*loc. cit.*), furnishes two octoacetyl derivatives. The first form, melting at 228—229° and identical with that described by Franchimont and by Skraup, is produced when the sugar is treated with acetic anhydride and sulphuric acid; the second form, obtained when the acetylation is conducted in presence of anhydrous sodium acetate, melts at 196° and is converted instantaneously into the first form by

heating with acetic anhydride and sulphuric acid. With benzoyl chloride, the sugar yields only resinous products.

Cellose furnishes an amorphous *hexaphenylurethane*,

$$C_{12}H_{20}O_{10}(CONPh)_6,$$

at the same time losing a molecule of water; the *oxime* is amorphous and on hydrolysis furnishes a *glucoarabinose*.

Cellose is oxidised by nitric acid (sp. gr. 1·2) into saccharic acid and by bromine in water into *cellobionic acid*, $C_{12}H_{22}O_{12}$, which, on hydrolysis, yields dextrose and gluconic acid. The salts of cellobionic acid are amorphous and very soluble in water, but less so in alcohol.

T. A. H.

Starch. LÉON MAQUENNE (*Ann. Chim. Phys.*, 1904, [viii], 2, 109—134).—A *résumé* of work already published (compare Abstr., 1903, i, 679; this vol., i, 17, 227, 228, 294. Compare also Fernbach and Wolff, this vol., i, 211, 374).

M. A. W.

Compounds of Chromic Chloride with Substituted Ammonias. WILLIAM R. LANG and CHARLES M. CARSON (*J. Amer. Chem. Soc.*, 1904, **26**, 758—759. Compare Proc., 1903, 147).—The action of ethylamine on chromic chloride at 0—18° is very vigorous, and dark red crystals of the *compound* $Cr_2Cl_6,10EtNH_2,2H_2O$ are formed. The latter, when heated at 60°, forms the *compound* $Cr_2Cl_6,8EtNH_2,2H_2O$. Dimethylamine, diethylamine, trimethylamine, and triethylamine have no effect on chromic chloride. Ethylenediamine reacts violently with chromium chloride at 0—18° with the formation of dark red crystals of the *compound* $Cr_2Cl_6,8C_2H_4(NH_2)_2,2H_2O$. Aniline, methylaniline, and dimethylaniline have no action on chromic chloride.

A. McK.

Density of Asparagine. ARNALDO PIUTTI (*Gazzetta*, 1904, **34**, ii, 36—46).—Boggio (*Gazzetta*, 1888, **18**, 477) stated that the sp. gr. of *l*-asparagine was 1·548, whilst that of the *d*-isomeride was 1·528 at the same temperature (about 14°/4°). As, however, both Liebisch and Walden found, as the result of the investigation of many optically active compounds, that the specific gravities of optical antipodes are always the same and in general different from that of the racemic compound, the author has made fresh measurements of *d*- and *l*-β-asparagines and of *i*-α-asparagine by the suspension method in a special apparatus; the liquid used was a mixture of bromoform and toluene. It is found that the *d*- and *l*-β-asparagines have the same sp. gr., namely, 1·5434 at 14·8°/4°. The value for *i*-α-asparagine at 14·8°/4° is 1·454.

T. H. P.

Cyanoacetylcyanamide. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 151597).—The potassium and sodium derivatives of ethyl cyanoacetate react very readily with an alcoholic solution of cyanoamide, forming *cyanoacetylcyanamide*, $CN\cdot CH_2\cdot CO\cdot NH\cdot CN$, which crystallises from ether in prisms and melts and decomposes at 93°. It dissolves readily in water, alcohol, or ether, and forms stable, neutral salts with alkalis. Cyanoacetylcyanamide may be employed for the synthesis of pyrimidine derivatives.

C. H. D.

Dimethylpyroarsonic Acid. E. BAUD (*Compt. rend.*, 1904, 139, 411—413).—When anhydrous methylarsonic acid is heated at 130—140° in a current of hydrogen, dimethylpyroarsonic acid is formed: $2H_2MeAsO_3 = H_2Me_2As_2O_5 + H_2O$ ($-5\cdot207$ Cal). The heat of solution of the acid in water is $-0\cdot513$ Cal. Heated at 170—180° in a current of hydrogen, the acid decomposes into methyl alcohol and arsenious oxide, $H_2Me_2As_2O_5 = 2MeOH + As_2O_3$. When sodium hydrogen methylarsonate is heated, it loses its water of crystallisation and then yields disodium dimethylpyroarsonate. Disodium methylarsonate heated at 140° in a current of carbon dioxide slowly absorbs the gas with formation of sodium carbonate and disodium dimethylpyroarsonate, $2Na_2MeAsO_3 + CO_2 = Na_2Me_2As_2O_5 + Na_2CO_3$.

H. M. D.

Action of Formaldehyde on Naphtha and its Distillation Products. ALEXANDER M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 881—898).—The action of formaldehyde on naphtha in presence of concentrated sulphuric acid yields a compound to which the author gives the name *formolite*. This compound is formed mainly from the less volatile fractions, whilst "benzine" (b. p. up to 100°) gives no trace of it. Formolite has the following percentage composition: C, 78·99; H, 7·39; O, 10·95; S, 2·67. It has a yellow or yellowish-brown colour and is amorphous, infusible, and insoluble in the ordinary solvents.

The amount of this compound formed from any sample of crude naphtha or any of its distillation products affords a new means of characterising these substances, the experiment being carried out as follows. Into an ordinary 100 c.c. measuring cylinder are placed a known volume (20—30 c.c.) of the oil and an equal volume of concentrated sulphuric acid, and to the mixture is added half its volume of formaldehyde solution. The whole is then shaken and the tap opened from time to time to admit of the escape of air and other gases; if necessary, the vessel is cooled with water. The mass is diluted with a large quantity of water, and poured into excess of ammonia solution, the solid product being filtered off and washed, firstly with water and afterwards with benzine. It is best to express the main bulk of the contained liquid, for example, by means of a small wine-press; the residual solid is broken up, pressed between filter paper if necessary, and left to dry in the air until of constant weight. The weight of formolite obtained, expressed as a percentage of the weight of oil taken, is the "formolite number."

As formolite is not obtained from the paraffin hydrocarbons, this reaction may be used to separate the latter from unsaturated cyclic hydrocarbons which do yield it.

The reaction may also be used for testing the purity of hydrocarbons and for preparing new hydrocarbons from the naphthylenes and terpenes (compare Abstr., this vol., i, 242). T. H. P.

Butylbenzenes. EYVIND BOEDTKER (*Bull. Soc. chim.*, 1904, [iii], 31, 965—971).—*tert.*-Butyl alcohol having n_D 1·38888 at 18·5° and 1·38705 at 25° (compare Brühl, Abstr., 1888, 781) was converted into the corresponding chloride (n_D = 1·38686 at 17·8°), and this was con-

densed with benzene in presence of aluminium chloride; the sole product was *tert.*-butylbenzene, which boiled at 168·2° under 760 mm. pressure and had n_D 1·49724 at 18·5°.

*iso*Butyl alcohol furnished a mixture of *iso*butyl and *tert.*-butyl chlorides (compare Freund, Abstr., 1876, i, 543), and this, when condensed with benzene, yielded principally *tert.*-butylbenzene. In addition, three fractions were obtained boiling at 170—172°, 173—174°, and 182—185°, which are in close agreement with the boiling points assigned to *iso*butylbenzene (Schramm, Abstr., 1889, 127), *sec.*-butylbenzene (Estreicher, Abstr., 1900, i, 213), and *n*-butylbenzene respectively. Determinations of the refractive indices of the three fractions and the observation that a mixture of the two lower fractions was partially converted into *tert.*-butylbenzene when heated with benzene and aluminium chloride, however, led the author to the conclusion that these three fractions consisted essentially of *iso*butylbenzene. When *iso*butyl alcohol is condensed with benzene by means of sulphuric acid (Verley, Abstr., 1899, i, 424), *tert.*-butylbenzene is the principal product, but there is also formed some *p*-di-*tert.*-butylbenzene identical with that prepared by Baur (Abstr., 1894, i, 446. Compare Verley, *loc. cit.*). This, on oxidation with chromic acid, yields *p*-butylbenzoic acid and 2 : 5-*di*-tert.-*butylbenzoquinone.* The latter crystallises from boiling alcohol in lemon-yellow leaflets, melts at 152·5°, sublimes easily and distils in steam. When treated with hydroxylamine hydrochloride in alcohol, it furnishes a *monoxime*, which separates from alcohol or light petroleum in pale yellow crystals and melts at 209°. On reduction, the quinone furnishes only resinous products, and, similarly, no definite substance could be isolated as the result of its interaction with magnesium methyl iodide. The formation of the quinone is stated to be the first recorded instance in which carbon atoms in a benzenoid nucleus have undergone oxidation in preference to those in lateral groups. T. A. H.

Derivatives of Trichlorotrinitrobenzene. C. Loring Jackson and Paul Shortt Smith (*Amer. Chem. J.*, 1904, 32, 168—181).—When 1 : 3 : 5-trichloro-2 : 4 : 6-trinitrobenzene is treated with an alcoholic solution of sodium ethoxide, trinitrophloroglucinol and its triethyl ether are produced.

Ethyl dichlorotrinitrophenylacetate, $C_6Cl_2(NO_2)_3·CH_2·CO_2Et$, obtained by the action of ethyl sodiomalonate on trichlorotrinitrobenzene, crystallises in groups of long, slender, white prisms, melts at 130—131°, and is freely soluble in benzene, chloroform, or acetone. When this ester is heated with aniline, *ethyl dianilinotrinitrophenylacetate*, $C_6(NHPh)_2(NO_2)_3·CH_2·CO_2Et$, is produced, which crystallises in long, slender, red prisms, melts at 201°, and is soluble in acetone, chloroform, or hot benzene, and insoluble in water; it unites with benzene to produce the additive *compound*, $C_6(NHPh)_2(NO_2)_3·CH_2·CO_2Et,2C_6H_6$, which forms golden-yellow crystals. If ethyl dichlorotrinitrophenylacetate is heated with concentrated hydrochloric acid at 150—160° in a sealed tube, 3 : 5-*dichloro*-2 : 4 : 6-*trinitrotoluene* is produced, which crystallises in long, slender, flat, white prisms, melts at 200—201°,

and is soluble in benzene, acetone, chloroform, or hot alcohol, and insoluble in water.

By the action of ethyl sodiomalonate on ethyl dichlorotrinitrophenylacetate, a substance is obtained which crystallises in white needles, melts at 147—148°, is soluble in benzene, chloroform, acetone, ether, carbon disulphide, or hot alcohol, and is probably *ethyl chlorotrinitrophenyleneacetic malonate*,

$$CO_2Et\cdot CH_2\cdot C_6Cl(NO_2)_3\cdot CH(CO_2Et)_2.$$

If this compound is heated with strong hydrochloric acid at 160—170° in a sealed tube, 5-chloro-2 : 4 : 6-trinitro-*m*-xylene (m. p. 215—220°) is produced (compare Klages and Knoevenagel, Abstr., 1895, i, 654).

E. G.

Constitution of β-Phenylacenaphthylmethane and its Oxidation Products; β-Benzyl- and β-Benzoyl-naphthalic Acids. CHARLES DZIEWONSKI and MARCUS WECHSLER (*Bull. Soc. chim.*, 1904, [iii], 31, 922—925. Compare this vol., i, 390).—It is now shown that the benzoylnaphthalic acid produced by the oxidation of the phenylacenaphthylmethane already described (*loc. cit.*) is a β-derivative. From this observation, it follows that in the parent hydrocarbon the benzyl group must occupy position 1 or 2 in the acenaphthene nucleus. The readiness with which phenylacenaphthylmethane is dehydrogenated by sulphur, forming tribenzyldecacyclene as one product (see succeeding abstract), leads the authors to regard position 2 as the more probable location of the benzyl group. On this supposition, the oxidation products are the 3-benzylnaphthalic and 3-benzoylnaphthalic acids.

T. A. H.

Synthesis of a New Yellow Hydrocarbon, Tribenzyldecacyclene (Tribenzyltrinaphthylenbenzene), and of a Red Thiophen Derivative, Dibenzyldinaphthylenthiophen. CHARLES DZIEWONSKI (*Bull. Soc. chim.*, 1904, [iii], 31, 925—932. Compare this vol., i, 84, 390, and preceding abstract).—[With ELIGIO DOTTA.]—The following substances are simultaneously produced when a mixture of 2-phenylacenaphthylmethane with sulphur is heated as already described (Abstr., 1903, i, 431).

Dibenzyldinaphthylenthiophen, $CH_2Ph\cdot C_{10}H_5<\begin{matrix} C\text{—}C \\ \| \quad \| \\ C\cdot S\cdot C \end{matrix}>C_{10}H_5\cdot CH_2Ph$,

crystallises from benzene in small, bright red needles, melts at 207—210°, is soluble in chloroform and in boiling benzene and its homologues, and slightly so in ether and alcohol; the solution in cold sulphuric acid is violet. It does not form an additive product with picric acid. Chromic acid oxidises it to 3-benzoylnaphthalic acid, indicating that in the parent substance a benzyl group occupies either the 3- or 6-position in each of the naphthalene nuclei.

Tribenzyldecacyclene, $C_6[C_{10}H_5\cdot CH_2Ph]_3$, crystallises from benzene or aniline in small, yellow needles, melts at 270°, and is almost insoluble in alcohol, ether, or boiling acetic acid; dilute solutions show a strong green fluorescence; the solution in sulphuric acid is green. The hydrocarbon does not form an additive product with picric acid. On

oxidation with chromic acid in presence of acetic acid, a brown, amorphous substance is formed. T. A. H.

Benzoylacenaphthene. GUSTAVE PERRIER (*Bull. Soc. chim.*, 1904, [iii], 31, 859—862. Compare Abstr., 1900, i, 331).—The author points out that this compound and its derivatives, recently obtained by Graebe and Haas (Abstr., 1903, i, 409), had already been described by Louïse and himself (Abstr., 1892, 1205, and *Thèse inaug.*, Paris, 1896). T. A. H.

Triphenylmethane Dyes from Dimethyl- and Diethyl-*p*-toluidines. LEOPOLD CASSELLA & Co. (D.R.-P. 149322).—Tetra-alkyldiaminobenzhydroles condense with dialkyl-*p*-toluidines in presence of concentrated sulphuric acid, and by oxidising the resulting leucobases, brilliant bluish-green dyes are obtained. *p*-Toluidine and its monoalkyl derivatives yield only dull shades. The methane carbon atom in the new derivatives probably occupies the *meta*-position to the dialkylamino-group. C. H. D.

Detection of Aldehydic Compounds; Constitution of Nitrosodimethylaniline. GIUSEPPE VELARDI (*Gazzetta*, 1904, 34, ii, 66—74).—The author finds that the reaction described by Angeli and Angelico (this vol., i, 172; ii, 115) and by Rimini (Abstr., 1901, i, 450), in which a compound capable of giving up the NOH-group acts on an aldehyde, is applicable generally and may be used for the detection of unsaturated aldehydes in complex mixtures such as natural oils. The hydroxamic acid formed is not, however, the only product, as the free NOH-group acts simultaneously on the double linking of the unsaturated aldehyde, forming the corresponding oxime; the yield of the latter increases with the number of double linkings in the molecule. Mixed aldehydes behave, in this reaction, similarly to the unsaturated ones, and the same is the case with nitroso-compounds, the constitution of which may be determined in this way.

The method adopted by the author for detecting the presence of an aldehyde in a natural oil is to mix a few drops of the oil with a trace of benzenesulphohydroxamic acid and alcoholic potassium hydroxide and heat the mixture; after cooling, the mass is diluted with water and a little ether added, the aqueous liquid being then neutralised with hydrochloric acid and tested with ferric chloride. Of a number of vegetable oils examined in this way by the author, the majority developed red colorations and a few gave yellow ones. Some of the salts of the hydroxamic acids are described.

Copper cinnamylhydroxamate, $CHPh{:}CH{\cdot}C{<}^{-O-}_{NO}{>}Cu$, is precipitated from solution in 25 per cent. sulphuric acid by means of sodium acetate in minute, emerald-green crystals.

Citronellalhydroxamic acid,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}C(OH){:}NOH,$$

is deposited from light petroleum in white crystals melting at 72—74°. The *copper* salt, $C_{10}H_{17}O_2NCu,2H_2O$, forms a green, crystalline powder.

Geranylhydroxamic acid, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}C(OH){:}NOH$, is a heavy oil; its *copper* salt, $C_{10}H_{15}O_2NCu$, was analysed.

Copper glycolhydroxamate, $OH{\cdot}CH_2{\cdot}C{<}^{-O-}_{NO}{>}Cu$, is precipitated from solution in dilute sulphuric acid by means of sodium acetate in minute, dark green crystals.

The *barium* salt of *dimethylaminonitrosophenylhydroxylamine*,

$$[NMe_2{\cdot}C_6H_4{\cdot}N(NO){\cdot}O]_2Ba,$$

separates from aqueous solution in minute, faintly yellow crystals.

T. H. P.

Protocatechuic Anilide. PAUL THIBAULT (*Bull. Soc. chim.*, 1904, [iii], 31, 920—922).—Protocatechuic acid (30 grams) is heated with aniline (60 grams) at 100° until solution is complete; phosphorus oxychloride (15 grams) is then added gradually and the mixture is heated at 150° until hydrogen chloride is no longer evolved. The anilide is extracted with an aqueous solution of sodium carbonate. It forms prismatic crystals, melts at 154—156°, and is soluble in alcohol, ether, and chloroform. At 180°, it is resolved into its generators.

The method suggested by Schiff (Abstr., 1883, 335) for the preparation of protocatechuic anilide yields an impure product containing arsenic.

T. A. H.

Action of Acid Chlorides on Tertiary Bases containing an Aromatic Radicle. VICTOR AUGER (*Compt. rend.*, 1904, 139, 299—301. Compare Hess, Abstr., 1885, 783).—At temperatures between 200° and 250°, the aliphatic acid chlorides react quantitatively with tertiary bases of the type $NR^IR^{II}R^{III}$ to form the substituted acid amide and alkyl chloride according to the equation $NR^IR^{II}R^{III} + RCOCl = RCONR^IR^{II} + R^{III}Cl$, where R^I and R represent aromatic and aliphatic radicles respectively, R^{II} having a lower molecular weight than R^{III}. *Acetylbenzylanilide*, $COMe{\cdot}NPh{\cdot}CH_2Ph$, obtained by the gradual addition of acetyl chloride to dibenzylaniline at 200°, forms colourless, tabular crystals melting at 58°, slightly soluble in boiling water or cold light petroleum, and very readily soluble in other neutral solvents. Acetylethylanilide is similarly prepared from benzylethylaniline. *Methylvaleranilide*, $CHMe_2{\cdot}CH_2{\cdot}CO{\cdot}NPhMe$, obtained by heating a mixture of *iso*valeryl chloride and dimethylaniline at 220°, boils at 170° under 50 mm. pressure and forms large crystals melting at 22°, is insoluble in water and very soluble in other neutral solvents, and is identical with the compound obtained by the action of *iso*valeryl chloride on a molecular mixture of pyridine and methylaniline. Attempts to replace the second aliphatic radicle of the base by a second acyl radicle were unsuccessful.

M. A. W.

Alkyl Esters of 3 : 4-Diaminobenzoic Acid. EDUARD RITSERT and WILHELM EPSTEIN (D.R.-P. 151725).—The aminocarboxylic esters are employed with difficulty as local anæsthetics on account of their insolubility, and their soluble salts react so strongly acid as to be unsuitable (compare this vol., i, 413, 414). The solubility and basicity of the esters is greatly increased by the introduction of a second amino-group.

Ethyl p-*acetylaminobenzoate*, prepared by acetylating ethyl *p*-amino-

benzoate, melts at 110°, and on nitration yields ethyl 3-nitro-4-acetylaminobenzoate, melting at 96—97° (compare Thieme, Abstr., 1891, 915). Alcoholic hydrogen chloride hydrolyses this to ethyl *m*-nitro-*p*-aminobenzoate, melting at 136° (compare Grohmann, Abstr., 1890, 305, and Thieme, *loc. cit.*). Alcoholic stannous chloride reduces this to *ethyl* 3 : 4-*diaminobenzoate*, crystallising from hot water in bundles of white needles and melting at 112—113°. It dissolves in 1/4 of the theoretical quantity of hydrochloric acid, the solution having only a faintly acid reaction. *p*-Aminobenzoic acid may be acetylated by heating its sodium salt with glacial acetic acid, and then nitrated. After hydrolysis and reduction, the product is readily esterified by warming with hydrogen chloride and methyl alcohol, yielding *methyl* 3 : 4-*diaminobenzoate*, crystallising in white needles, melting at 108—109°, and dissolving more readily in cold water than the ethyl ester. C. H. D.

Acetyl-*p*-aminophenylglycine. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 152012).—Acetylphenylglycine does not yield a nitro-derivative with nitric acid alone (Paal and Otten, Abstr., 1890, 1415), but is readily nitrated in sulphuric acid solution at 0—5°. *Acetyl-*p*-nitrophenylglycine* crystallises from glacial acetic acid in light brown leaflets, melts at 191—192°, and dissolves in alkalis to a pale yellow solution. Iron and dilute acetic acid reduce it on warming to *acetyl*-p-*aminophenylglycine*, which is very readily soluble in water and cannot be isolated in the solid state. Its diazonium compound is pale yellow, and forms a crimson dye with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. C. H. D.

Preparation of Acetylphenylglycine-*o*-carboxylic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 151435. Compare Abstr., 1901, i, 709).—The salts of phenylglycine-*o*-carboxylic acid are partly converted into indoxyl derivatives by heating with acetic anhydride. The acetyl derivative is, however, obtained quantitatively on adding acetic anhydride in cold aqueous suspension to the acid salts. C. H. D.

Orthophosphoric Anilide and its Homologues; Non-existence of the Compound $NHPh{\cdot}P(NPh)_2$. PAUL LEMOULT (*Compt. rend.*, 1904, 139, 206—208).—The chlorotetra-anilides, $PCl(NHR)_4$, which are formed by the prolonged action of phosphorus pentachloride on the amines (compare Abstr., 1897, i, 463), readily lose hydrochloric acid on boiling with alcoholic potash, anilides of phosphoric acid and primary amines resulting according to the equations : (1) $PCl(NHR)_4 = P(NHR)_3{:}NR + HCl$; (2) $P(NHR)_3{:}NR + H_2O = PO(NHR)_3 + NH_2R$. When sodium ethoxide in absolute alcohol is used instead of alcoholic potash, the second reaction cannot take place, and the product obtained is the intermediate compound, $P(NHR)_3{:}NR$.

The substance obtained by Gilpin (Abstr., 1902, i, 700) by the action of phosphorus pentachloride on aniline dissolved in benzene and treatment of the product with boiling water, to which he assigned

the formula $P(NPh)_2 \cdot NHPh$, is, in reality, orthophosphoric anilide, $PO(NHPh)_3$, melting at 212°.

The homologue obtained from *m*-xylidine crystallises in large, silky needles melting at 225°.

On heating the anilide and its homologues somewhat above their respective melting points, they lose a molecule of the amine and probably yield substances of the type $PO(NR) \cdot NHR$. H. M. D.

Some Derivatives of Pentabasic Phosphoric Acid, $P(OH)_5$. P. Lemoult (*Compt. rend.*, 1904, 139, 409—411. Compare this vol., i, 380).—The reaction between the chlorotetra-anilides of the type $PCl(NHR)_4$ and the sodium alkyloxides depends on the nature of the radicle R. If R is the phenyl group, trianilinophenylphosphimide, $P(NPh)(NHPh)_3$, is obtained whichever alkyloxide is employed. If R is a homologue of phenyl, the products obtained vary with the nature of the alkyloxide, but can be represented by the general formula $P(OR^1)(NHR)_4$, where R^1 is the radicle of the alkyloxide.

To obtain these substances, phosphorus chlorotetra-anilide is suspended in boiling alcohol, and the calculated quantity of the corresponding sodium alkyloxide is added; the hot solution is then filtered and allowed to crystallise. The analysis of the products, and the action of hydrochloric acid on them, indicate that alcohol of crystallisation is present.

The *compound* $P(NH \cdot C_6H_4Me)_4 \cdot OEt,EtOH$ forms large, white crystals melting at 114°, at which temperature decomposition takes place.

The *compound* $P(NH \cdot C_6H_3Me_2)_4 \cdot OMe,MeOH$ is obtained in the form of lustrous spangles or in crystals melting at 98° and resembling the preceding compound.

The *compound* $P(NH \cdot C_6H_3Me_2)_4 \cdot OEt,EtOH$ forms fine needles melting at 107°. These substances are soluble in hot alcohol, are decomposed by boiling acetic acid and benzene, and are saponified by alkalis. By the action of hydrochloric acid in alcoholic solution, the original chlorotetra-anilide is obtained. H. M. D.

Decomposition of Nitroso-compounds. William A. Noyes and René de M. Taveau (*Amer. Chem. J.*, 1904, 32, 285—293).—The nitroso-compound prepared from aminolauronic anhydride, and melting at 138—139° (Bredt, Abstr., 1902, i, 374), is decomposed by cold sodium hydroxide and alcohol, forming a hydrocarbon, C_8H_{14}, *iso*lauronolic acid, $C_8H_{14} \cdot CO_2H$, a hydroxy-acid, a lactone, and a condensation product.

The hydroxy-acid, $OH \cdot C_8H_{14} \cdot CO_2H$, boils at 180—185° under 25 mm. pressure and is identical with that prepared from ethyl aminolauronate and nitrous acid. The lactone is *iso*campholactone, $C_8H_{14}{<}\genfrac{}{}{0pt}{}{CO}{O}$, melting at 32° (compare Abstr., 1895, i, 295, and Bredt, *loc. cit.*). A 5 per cent. alcoholic solution has $[\alpha]_D - 60 \cdot 7°$. The silver salt of the corresponding acid, $OH \cdot C_8H_{14} \cdot CO_2Ag$, was prepared.

The *condensation product*, $\left(C_8H_{14}{<}\genfrac{}{}{0pt}{}{CO}{N \cdot C_2H_4O}\right)_2$, crystallises from

light petroleum in large, faintly yellow plates and melts at 140°. It is almost insoluble in water, but dissolves in dilute hydrochloric acid and is reprecipitated by ammonia. When methyl alcohol is used in the preparation instead of ethyl alcohol, a *compound*, $(C_{10}H_{16}O_2N)_2$, crystallising from light petroleum in leaflets and melting at 99° is obtained. The molecular weight was determined cryoscopically in benzene solution. The reaction has some analogy with the formation of acetaldehyde from diazonium compounds and ethyl alcohol.

On filtering off the condensation product obtained from sodium hydroxide, methyl alcohol, and the nitroso-compound and acidifying, a white, dibasic acid, probably $CO_2H{\cdot}C_8H_{14}{\cdot}N{:}N{\cdot}C_8H_{14}{\cdot}CO_2H$, melting at 327—328° (corr.), is obtained. C. H. D.

Preparation of Nerol from Petit Grain Oil. HEINE & Co. (D.R.-P. 150495.)—The terpene alcohol, nerol, $C_{10}H_{18}O$, obtained by Hesse and Zeitschel from neroli oil (Abstr., 1903, i, 189) may also be prepared from petit grain oil. The oil is saponified and distilled with steam or under reduced pressure, and after removal of terpenes and linalool the following fraction is converted into the phthalic ester and purified. After hydrolysis, a mixture of 40 per cent. nerol and 60 per cent. geraniol is obtained. The geraniol is separated by means of dry calcium chloride, and the nerol thus obtained is rectified. Nerol is optically inactive and forms an additive compound with four atoms of bromine. Its physical properties are identical with those of the nerol prepared from neroli oil. C. H. D.

Preparation of Vanillin. F. FROGER-DELAPIERRE (D.R.-P. 150981).—In the oxidation of eugenol or *iso*eugenol by ozone, resin is generally produced. This is avoided and a good yield of vanillin obtained by using air previously rendered active by passing through a terpene, sesquiterpene, or similar hydrocarbon. Thus the air may be caused to bubble through a layer of turpentine at 30—35°, then to pass through a plate-column at 80—90°, and finally over a layer of *iso*eugenol heated at 100°, and rendered neutral or slightly alkaline. When phenols containing an allyl group are to be oxidised, a mixture of 1 vol. of oxygen with 2 vols. of carbon dioxide is to be employed in preference to air. C. H. D.

Isomeric Ethers of Pyrogallol. II. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1904, 25, 501—519. Compare Abstr., 1903, i, 89, 346; Graebe and Martz, Abstr., 1903, i, 262).—2 : 3-*Dihydroxy-4-methoxybenzene-1-carboxylic acid*, obtained by hydrolysis of its methyl ester, crystallises in long, white needles and melts at 204—206°. When heated at 230°, the acid loses carbon dioxide and yields 1-*methoxy-2 : 3-dihydroxybenzene*, which crystallises in needles, melts at 37—40°, and boils at 146—147° under 15—16 mm. pressure. The *diacetyl* derivative, $C_6H_3(OMe)(OAc)_2$, crystallises in white leaflets and melts at 91—93°.

On oxidation, 2 : 3-dimethoxyphenol, unlike its 2 : 6-isomeride, gives no cœrulignone reaction. The *benzoyl* derivative of 2 : 3-dimethoxy-

phenol crystallises in long, colourless needles and melts at 55—57°; the benzoyl derivative of 2 : 6-dimethoxyphenol melts at 118°.

In the formation of 2-hydroxy-3 : 4-dimethoxybenzene-1-carboxylic acid, a small amount of 2 : 3 : 4-trimethoxybenzene-1-carboxylic acid is formed. 1 : 2 : 3-Trimethoxybenzene is formed by the action of methyl iodide and potassium hydroxide on 2 : 3-dimethoxyphenol in aqueous methyl-alcoholic solution. G. Y.

4-Formylamino-α-naphthol. FRANZ GAESS (D.R.-P. 149022).—4-Amino-α-naphthol is readily formylated by heating the hydrochloride with sodium formate and concentrated formic acid. The hydroxyl group is not attacked. *4-Formylamino-α-naphthol* crystallises from water in rosettes of small, colourless needles, melts at 168°, and dissolves readily in alcohol. The acetyl group cannot be introduced in the same manner, the use of acetic anhydride being necessary.

C. H. D.

Disazo-dyes from 6-Amino-α-naphthol-3-sulphonic Acid. K. OEHLER (D.R.-P. 151332).—The azo-compounds prepared by combining diazonium salts with 6-amino-α-naphthol-3-sulphonic acid react in alkaline solution with diazotised nitro-derivatives of *o*-aminophenol to form disazo-dyes. *o*-Diazophenol does not combine, but any of its derivatives containing at least one nitro-group may be employed. The preparation of dyes from picramic acid and from 3-nitro-5-amino-4-hydroxybenzoic acid is described. C. H. D.

Acyl Derivatives of Alkyl Ethers of Rufigallol. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 151724).—The acyl derivatives of rufigallol possess purgative properties. *Diacetylrufigallol tetramethyl ether*, $C_{22}H_{20}O_{10}$, crystallises from acetic acid or alcohol in yellow masses and melts at about 180—190°. It is insoluble in water, but dissolves sparingly in alcohol. *Diacetylrufigallol tetraethyl ether*, $C_{26}H_{28}O_{10}$, separates from chloroform and alcohol in yellow crystals and melts at 230—235°. *Benzoylrufigallol tetramethyl ether*, prepared by alkaline benzoylation, is precipitated from chloroform solution by alcohol as a brown powder and melts at 190—205°.

C. H. D.

Synthesis of Alcohols of the *cyclo*Hexane Series. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1904, **139**, 343—346).—Magnesium *cyclo*hexyl chloride, obtained by the action of magnesium on *cyclo*hexyl chloride in presence of iodine readily reacts with aldehydes and ketones, giving a crystalline mass which is decomposed by water with the production of alcohols of the *cyclo*hexane series. The alcohols thus produced lose water on heating with anhydrous zinc chloride, and unsaturated hydrocarbons are obtained.

*cyclo*Hexylcarbinol, $C_6H_{11}\cdot CH_2\cdot OH$ (compare Abstr., 1903, i, 673), is obtained from trioxymethylene; it has an odour resembling that of camphor, boils at 181° under 755 mm. pressure, has a sp. gr. 0·944 at 0°/0°. The hydrocarbon, $C_6H_{10}{:}CH_2$, which it yields, boils at 105°, and has a sp. gr. 0·828 at 0°/0°. By action of ethyl orthoformate on magnesium *cyclo*hexyl chloride in ethereal solution, a solid mass is obtained

which with water gives the acetal, $C_6H_{11}\cdot CH(OC_2H_5)_2$, an oily liquid boiling at 109—110° under 20 mm. pressure. When boiled with dilute sulphuric acid, it yields the aldehyde, $C_6H_{11}\cdot COH$, a liquid boiling at 155·5° under 755 mm. pressure.

*cyclo*Hexylmethylcarbinol, $C_6H_{11}\cdot CHMe\cdot OH$, previously obtained by Bouveault (compare this vol., i, 61), is a liquid boiling at 189° under 755 mm. pressure, and having a sp. gr. 0·9456 at 0°/0°. The hydrocarbon, $C_6H_{10}\colon CH\cdot CH_3$, boils at 135°, sp. gr. 0·842 at 0°.

cyclo*Hexylisobutylcarbinol*, $C_6H_{11}\cdot CH(OH)\cdot CHMeEt$, is obtained from *iso*valeraldehyde; it is a liquid boiling at 123° under 20 mm. pressure, sp. gr. 0·916 at 0°/0°. On oxidation with chromic acid, it yields the ketone, $C_6H_{11}\cdot CO\cdot CHMe_2$, boiling at 114° under 20 mm. pressure. The corresponding oxime melts at 77°.

cyclo*Hexyldimethylcarbinol*, $C_6H_{11}\cdot CMe_2\cdot OH$, the product obtained from acetone, is a liquid of strong camphoraceous odour which boils at 96° under 20 mm. pressure and has a sp. gr. 0·938 at 0°/0°. The corresponding hydrocarbon, $C_6H_{10}\colon C(Me)_2$, boils at 151° under 760 mm. pressure and has a sp. gr. 0·864 at 0°/0°.

Benzaldehyde yields *phenyl*cyclo*hexylcarbinol*, $C_6H_{11}\cdot CHPh\cdot OH$, a crystalline solid melting at 41° and boiling at 168° under 20 mm. pressure, very soluble in alcohol and ether. The hydrocarbon, $C_6H_{10}\colon CHPh$, boils at 138° under 20 mm. pressure and has a sp. gr. 0·982 at 0°/0°. On oxidising the alcohol, the ketone, $C_6H_{11}\cdot COPh$, melting at 51°, is obtained.

Acetophenone yields *phenyl*cyclo*hexylmethylcarbinol*,

$$C_6H_{11}\cdot CMePh\cdot OH,$$

a liquid boiling at 168° under 20 mm. pressure and having a sp. gr. 1·043 at 0°/0°; it yields the hydrocarbon, $C_6H_{10}\colon CMePh$, boiling at 159° under 36 mm., or at 260° under 755 mm. pressure, and has a sp. gr. 0·981 at 0°/0°.

Benzophenone behaves differently, the products resulting from the reaction being *cyclo*hexene and benzhydrol.

From ethyl formate, *di*cyclo*hexylcarbinol*, $CH(C_6H_{11})_2\cdot OH$, which melts at 63° and boils at 166° under 20 mm. pressure, is obtained. Chromic acid converts it into the ketone, $C_6H_{11}\cdot CO\cdot C_6H_{11}$, a liquid boiling at 159° under 20 mm. pressure, and having a sp. gr. 0·986 at 0°/0°. With magnesium *cyclo*hexyl chloride, the ketone does not give tri*cyclo*hexylcarbinol, but di*cyclo*hexylcarbinol and *cyclo*hexene are obtained. The hydrocarbon, $C_6H_{10}\colon CH\cdot C_6H_{11}$, boils at 133° under 20 mm. pressure and has a sp. gr. 0·919 at 0°/0°. H. M. D.

Amino-derivatives of Hydroxybenzyl Alcohols. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 148977).—Aminohydroxybenzyl alcohols and their ethers and esters may be prepared by the reduction of nitrohydroxybenzyl alcohols and their ethers, or of the esters prepared by the action of acids on nitrohydroxybenzyl chlorides (Abstr., 1903, i, 338). *3-Amino-6-hydroxybenzyl alcohol*, $OH\cdot C_6H_3(CH_2\cdot OH)\cdot NH_2$, prepared by reducing the nitro-compound with tin and hydrochloric acid, crystallises from alcohol in colourless leaflets, becoming brown in air, and melts and darkens at 135—142°. The salts are stable. The *methyl ether* forms colourless leaflets, melts

at 124—126°, and dissolves sparingly in water. The *ethyl ether* is similar, and melts at 76—78°. 3-*Nitro-6-hydroxybenzyl acetate*, from the corresponding chloride with acetic acid and sodium acetate, crystallises from water in yellow needles and melts at 105—107°. 3-*Amino-6-hydroxybenzyl acetate* forms crusts of needles and leaflets and melts at 136—137°. 3-*Amino-2-hydroxybenzyl alcohol* forms colourless needles and melts at 112—114°. All these bases become brown in air, but form stable salts. C. H. D.

Condensation of Acetylenic Ketones with the Alcohols and Phenols. Charles Moureu and M. Brachin (*Compt. rend.*, 1904, 139, 208—210. Compare this vol., i, 286).—When phenylbutyrylacetylene, CPh:C·COPr^{a}, is treated with sodium ethoxide in ethyl alcohol, condensation takes place and ω-butyryl-α-ethoxystyrene,

OEt·CPh:CH·COPr^{a},

is formed; this melts at 137—138°, boils at 155—158° under 10 mm. pressure, and has a sp. gr. 1·013 at 20°/0°. The reaction takes place more readily, and a better yield is obtained if a little phenol is added to the alcohol. On warming with dilute sulphuric acid, the product is completely hydrolysed, and butyrlacetophenone, COPh·CH_2·COPr^{a}, is formed.

In a similar way, ω-propionyl-α-ethoxystyrene, OEt·CPh:CH·COEt, results from the condensation of propionylphenylacetylene with ethyl alcohol. It is a colourless oil, distils at 167—170° under 18 mm. pressure, and has a sp. gr. 0·972 at 20°/0°; on hydrolysis, it yields propionylacetophenone.

The phenols are found to react in the same manner. ω-Butyryl-α-phenoxystyrene, OPh·CPh:CH·COPr^{a}, crystallises from light petroleum in beautiful prisms, melts at 55°, boils at 206—209° under 11 mm. pressure, and yields butyrylacetophenone on hydrolysis. ω-Propionyl-α-guaiacyloxystyrene, OMe·C_6H_4·O·CPh:CH·COEt, is obtained by condensation of propionylphenylacetylene with guaiacol. It crystallises readily from light petroleum, melts at 76—77°, boils at 231° under 17 mm. pressure, and yields propionylacetophenone on hydrolysis (compare Abstr., 1903, i, 581). H. M. D.

Preparation of Organic Acids from Petroleum. Nicolai Zelinsky (D.R.-P. 151880).—The reaction between magnesium and chlorinated paraffins is very incomplete, but may be rendered complete by the addition of a catalytic agent, such as iodine, aluminium haloids, or hydrogen chloride. The fractions obtained in the distillation of petroleum may be converted into the corresponding carboxylic acids by chlorinating, adding magnesium and a catalytic agent, passing a current of carbon dioxide, and decomposing the complex magnesium compound thus obtained. The yield may amount to 60 per cent. of the theoretical. Pentane yields *iso*hexoic acid; a naphthene fraction boiling at 80—82° yields pure *cyclo*hexanecarboxylic acid, and a naphthene fraction boiling at 71—79° yields heptoic, methyl*cyclo*pentanecarboxylic, and *cyclo*hexanecarboxylic acids. C. H. D.

Action of Ethyl Oxalacetate on Benzaldehyde in Presence of Primary Amines. LOUIS J. SIMON and A. CONDUCHÉ (*Compt. rend.*, 1904, 139, 211—212).—Ethyl oxalacetate condenses with the aldehydes in the presence of ammonia, and substituted derivatives of diketodihydropyrrolinecarboxylic acid are obtained (compare this vol., i, 521). The same reaction takes place when the ammonia is replaced by primary fatty and aromatic amines. The substitution product obtained from aniline by warming a mixture of ethyl oxalacetate, benzaldehyde, and aniline in molecular proportions on the water-bath, or by acting in the cold on the oxalacetate with an alcoholic or ethereal solution of benzylideneaniline, melts at 173° and gives a phenylhydrazone melting at 150°. The product obtained from *p*-toluidine melts at 159°; *o*-toluidine apparently does not undergo this condensation. H. M. D.

Action of Ethyl Oxalacetate on Aromatic Aldehydes in the Presence of β-Naphthylamine. LOUIS J. SIMON and A. CONDUCHÉ (*Compt. rend.*, 1904, 139, 297—299. Compare this vol., i, 521).—Ethyl oxalacetate reacts with benzaldehyde and β-naphthylamine or with benzylidene-β-naphthylamine to form the *compound*

$$CO_2Et\cdot CO\cdot CH(CO_2Et)\cdot CHPh\cdot NH\cdot C_{10}H_7$$

and not a derivative of diketodihydropyrrolinecarboxylic acid, as stated by Schiff and Bertini (compare Abstr., 1897, i, 293). The new compound crystallises in white needles melting at 162°, loses H_2O on treatment with concentrated sulphuric acid to form a yellow or orange crystalline compound, $C_{25}H_{23}O_4N$, melting at 146—147°, which on oxidation with chromic acid is converted quantitatively into the compound $C_{25}H_{21}O_4N$, crystallising in white needles, melting at 128°, containing two carbethoxy-groups, and yielding on hydrolysis an acid, probably phenylnaphthaquinolinedicarboxylic acid, melting at 215—220°, and slightly soluble in boiling water or alcohol. By the action of alcoholic potassium hydroxide on the yellow compound melting at 146—147°, a basic compound, probably phenylnaphthaquinoline, melting at 189°, is obtained. Analogous compounds are obtained when the benzaldehyde is replaced by anisaldehyde or *m*-nitrobenzaldehyde, whilst piperonal yields a derivative of diketodihydropyrrolinecarboxylic acid; salicylaldehyde or vanillin gives a negative result. M. A. W.

Reduction of *o*-Quinones. FRANZ KNESCH (D.R.-P. 151981).—The reduction of *o*-quinones derived from polynuclear hydrocarbons to the corresponding *o*-dihydroxy-compounds by sulphur dioxide is incomplete, and when the reaction occurs under pressure partial decomposition often takes place. Almost pure products may be obtained by reducing the sodium hydrogen sulphite compounds of *o*-quinones by iron or zinc dust without the addition of acids or alkalis. Salts of hyposulphurous acid are formed, which act as reducing agents.

9 : 10-Dihydroxyphenanthrene, from phenanthraquinone, forms a *dibenzoyl* derivative melting at 230—231°. *Dihydroxychrysene*, from chrysoquinone, is white and melts at 152—154°, the *diacetyl* derivative melts at 225—228°, and the *dibenzoyl* derivative at 241—242°.

Dihydroxyretene forms a *diacetyl* compound melting at 170—171° and a *dibenzoyl* compound melting at 231—232°. C. H. D.

Electrolytic Oxidation of Organic Compounds. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 152063).—Many organic compounds may be electrolytically oxidised in a bath containing cerium salts. The ceric compound produced at the anode is at once reduced to cerous salt by the organic compound, so that in a well-conducted operation the solution remains colourless throughout. No diaphragm is necessary, and the compound to be reduced may be either in solution or in fine suspension.

Anthracene is best suspended in 20 per cent. sulphuric acid containing 2 per cent. of cerous sulphate and electrolysed with a current of 5 amperes per sq. dm. and a potential difference of 2·8—3·5 volts, the temperature being 80—90°, raised at the end to 100°. Naphthalene yields naphthaquinone and, on further oxidation, phthalic acid. Phenanthrene requires a more concentrated cerium solution, and yields phenanthraquinone, or, on further oxidation, diphenic and benzoic acids. C. H. D.

Chloro-derivatives of β-Hydroxyanthraquinones. R. Wedekind & Co. (D.R.-P. 152175).—Alkaline solutions of hypochlorites oxidise alizarin and other hydroxyanthraquinone dyes, and also the non-dyeing α-hydroxyanthraquinones, such as anthrarufin, almost instantaneously. On the other hand, the non-dyeing β-hydroxyanthraquinones are converted by this treatment into chloro-derivatives: $RH + NaOCl = RCl + NaOH$. Monochloro-derivatives are generally obtained in strongly alkaline solution; in presence of alkali carbonates, higher substituted derivatives may be obtained. A temperature of 30—40° is desirable, some alkali hydrogen carbonate being added to fix the alkali hydroxide formed. Anthraflavic acid yields, according to the conditions of experiment, a mono-, di-, or trichloro-derivative. The preparation of *dichloro*iso*anthraflavic acid* and of *chloro-β-hydroxyanthraquinone* is also described. On fusion, chlorine and hydrogen chloride are evolved, but the chlorine is nevertheless firmly combined, not being removed, in the case of trichloroanthraflavic acid, by heating for 14 hours at 220° with milk of lime.

C. H. D.

[Bromo-derivatives of Arylaminoanthraquinones.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 151512 and 151513).—2 : 4-*Dibromo*-5-*nitro*-1 *aminoanthraquinone*, prepared by brominating 5-nitro-1-aminoanthraquinone in water, crystallises from pyridine or nitrobenzene in short, thick, red needles and is insoluble in water, alkalis, or dilute acids. It condenses with *p*-toluidine in presence of sodium acetate, yielding 2-*bromo*-1-*amino*-4 : 5-*di*-p-*toluidinoanthraquinone*, which crystallises from pyridine in bronze needles. Other arylamino-groups may be introduced in the same manner. Soluble blue dyes are obtained on sulphonating these compounds with fuming sulphuric acid. C. H. D.

Introduction of Amine Residues into Hydroxyanthraquinones. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 151511).—Three aniline residues may be introduced into purpurin, hydroxyanthrapurpurin, or hydroxyflavopurpurin by heating with aniline and boric acid for 2 hours at 140—150°, and finally at 180—185° until the bluish-green colour becomes permanent.

Trianilinoanthraquinone crystallises from aniline or pyridine in black needles and dissolves in chloroform to a bluish-green solution. The product from hydroxyflavopurpurin and aniline forms metallic needles. The solutions in concentrated sulphuric acid are yellow, becoming red on warming. C. H. D.

Compound of Santalol and Formaldehyde. Alfred Stephan (D.R.-P. 148944).—Santalol combines with formaldehyde in presence of dilute mineral acids at 95—100°. The *compound*, $C_{16}H_{18}O_2$, formed is a yellow, balsam-like oil and has a sp. gr. 0·882 and $[\alpha]_D$ 10·9° at 20° in chloroform solution. Warm water on distillation decomposes it into santalol and formaldehyde. C. H. D.

Galloflavin and Resoflavin. Josef Herzig and Rudolf Tscherne (*Monatsh.*, 1904, 25, 603—610. Compare Bohn and Graebe, Abstr., 1887, 1167).—Analytical results obtained with galloflavin and its acetyl derivative agree with the formulæ $C_{15}H_8O_{10}$ and $C_{15}H_3O_5(OAc)_5$ better than with Bohn and Graebe's formulæ, $C_{13}H_6O_9$ and $C_{13}H_2O_5(OAc)_4$. The same acetyl derivative was obtained from galloflavin by Herzig and Pollak's method of acetylation (Abstr., 1901, i, 478).

The action of diazomethane on galloflavin suspended in ether leads to the formation of the *methyl* derivative, $C_{15}H_3O_5(OMe)_5$, which crystallises in yellow needles and melts at 235—237°.

Resoflavin, obtained by oxidation of 3 : 5-dihydroxybenzoic acid, yields an *acetyl* derivative, which melts at 274—277°, and, by the action of diazomethane, a yellow *methyl* derivative, which melts at 282—283°. Resoflavin and its derivatives closely resemble the galloflavin compounds. G. Y.

Ononin. III. Franz von Hemmelmayr (*Monatsh.*, 1904, 25, 555—582. Compare Abstr., 1902, i, 480; 1903, i, 508).—A molecular weight determination with ononetin shows that this substance has the formula $C_{18}H_{16}O_5$, which agrees with the formula $C_{25}H_{26}O_{11}$ for ononin.

Ononetin is precipitated by carbon dioxide from its solution in aqueous baryta; it dissolves in aqueous ammonia to a green solution, from which it slowly separates. A small part dissolves in aqueous potassium hydroxide to a green solution from which hydrochloric acid precipitates a black tar. Formononetin dissolves with more or less difficulty in 8 per cent. aqueous potassium hydroxide, from which it is reprecipitated as a jelly by the addition of sulphuric acid. The oxidation of formononetin with potassium permanganate in alkaline solution leads to the formation of anisic acid and of two *substances* which melt at about 74° and 155° respectively, and are methoxy-

compounds. If only a small quantity of potassium permanganate is used in the oxidation, no anisic acid is formed, but a *substance* is obtained which yields a *hydrazone* melting at 213—214°.

The action of boiling nitric acid (1-acid : 3-water) on formononetin leads to the formation of a crystalline *substance* melting at 186°, a *mixture* of substances melting at 150—155°, and a trinitrodihydroxybenzene, which melts at 163° and is isomeric with styphnic acid; it yields a *silver* salt, $C_6HO_8N_3Ag_2$. The action of bromine on formononetin in alkaline solution leads to the formation of a mixture of *bromo*-derivatives, which melts between 242° and 261°, but if the bromination is carried out in glacial acetic acid solution in a sealed tube at 125°, the white, crystalline compound obtained melts at 325° and approximates in composition to the formula $C_{19}H_9O_5Br_5$. When the mixture of bromo-derivatives of formononetin is boiled with 10 per cent. aqueous potassium hydroxide, it yields a *product* which crystallises in glistening scales, melts at 175—176°, and has a composition between $C_{18}H_{16}O_5Br_4$ and $C_{18}H_{15}O_5Br_3$.

The action of bromine on ononetin in chloroform solution leads to the formation of a *substance* which crystallises in colourless prisms; one preparation melted at 133—134° and became a clear liquid at 145°; a second preparation melted at 142—150°. The composition of both preparations lies between $C_{18}H_{16}O_5Br_2$ and $C_{18}H_{13}O_5Br_3$.

The author suggests that ononetin has the constitution:

$$\begin{array}{l}\mathrm{CH{\cdot}CH{=\!=}C{\cdot}C_5H_2(OH)_2{\cdot}C{=}CH{\cdot}CH} \\ \mathrm{C(OH){\cdot}CH{:}C{\cdot}OH \qquad\quad CH{:}CH{\cdot}C{\cdot}OMe.}\end{array}$$

G. Y.

Sulphonamido-derivatives of Furan. HENRY B. HILL and J. P. SYLVESTER (*Amer. Chem. J.*, 1904, 32, 185—228).—*Potassium 3-sulpho-5-methylpyromucate*, $C_6H_4O_6SK_2,2H_2O$, crystallises in slender prisms and becomes anhydrous at 130°. Phosphorus pentachloride, followed by ammonia, converts it into *3-sulphonamido-5-methylpyromucamide*, $NH_2{\cdot}SO_2{\cdot}C_4OHMe{\cdot}CO{\cdot}NH_2$, which crystallises from water in prisms, melts at 196—197°, and dissolves readily in alcohol, sparingly in chloroform; its aqueous solution is neutral to litmus. Alkali hydroxides convert it in the cold into *3-sulphonamido-5-methylpyromucic acid*, $C_6H_7O_5NS$, crystallising in rectangular prisms, melting at 217—218°, and dissolving readily in alcohol, sparingly in ether. The *potassium* salt contains H_2O, and the *barium* salt contains $3H_2O$; the *lead*, *calcium*, and *silver* salts are also described. Bromine oxidises solutions of the salts to *2-bromo-3-sulphonamido-5-methylfuran*,

$$C_4OHMeBr{\cdot}SO_2{\cdot}NH_2,$$

which crystallises from water in prisms, melts at 123°, and dissolves readily in alcohol or ether, sparingly in cold benzene or chloroform. Although neutral to litmus, it dissolves readily in dilute alkali hydroxides and is not decomposed on boiling. Acids precipitate it unchanged. Some sulphoacetylacrylic acid,

$$CH_3{\cdot}CO{\cdot}CH{:}C(SO_3H){\cdot}CO_2H,$$

is formed during the oxidation, especially when the bromine is in excess.

Potassium 5-chloro-3-sulphopyromucate (Hill and Hendrixson,

Abstr., 1893, i, 313) reacts with phosphorus pentachloride and ammonia to form 5-*chloro-3-sulphonamidopyromucamide*,

$$NH_2\cdot SO_2\cdot C_4HClO\cdot CO\cdot NH_2,$$

which crystallises from water in thick prisms and melts at 212°. Barium hydroxide converts it into 5-*chloro-3-sulphonamidopyromucic acid*, crystallising in prisms, melting at 194—195°, and dissolving readily in alcohol, sparingly in ether. The *potassium*, *barium*, *calcium*, *lead*, and *silver* salts are described. Bromine oxidises the salts to 5-*chloro-2-bromo-3-sulphonamidofuran*, $C_4H_3O_3NClBrS$, which crystallises from water in long needles, melts at 134—135°, and dissolves very readily in alcohol, sparingly in chloroform or benzene. It is a weak acid and forms salts with alkalis.

The action of phosphorus pentachloride on potassium 5-bromopyromucate (Hill and Sanger, Abstr., 1886, 446) results in the replacement of the bromine in the nucleus by chlorine. Phosphorus pentabromide, however, followed by ammonia, reacts to form 5-*bromo-3-sulphonamidopyromucamide*, crystallising in prisms, melting at 219—220°, and dissolving sparingly in cold water or alcohol, readily on heating. Barium hydroxide hydrolyses it to 5-*bromo-3-sulphonamidopyromucic acid*, which melts at 190—191° and dissolves readily in water or alcohol. The *potassium*, *barium*, *lead*, and *silver* salts are described. Bromine forms 2 : 5-*dibromo-3-sulphonamidofuran*, crystallising in long prisms and melting at 153·5°. The *potassium* salt crystallises from alcohol in glistening scales.

The derivatives of 3-sulphonamidopyromucic acid described are not converted into sulphimides on heating alone or with dehydrating agents. C. H. D.

Properties of Oxygen in the Pyran Ring. Dinaphthapyran (Dinaphthaxanthen) Series. ROBERT FOSSE (*Ann. Chim. Phys.*, 1904, [viii], 2, 233—284; 289—345).—A *résumé* of work already published (compare Abstr., 1901, i, 323, 384, 604, 643; 1902, i, 51, 171, 304, 368, 449, 689; 1903, i, 49, 357; this vol., i, 83, 519).

M. A. W.

Preparation of Indole. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 152683).—Indole may be prepared by heating phenylglycine or its derivatives, such as phenylglycine-*o*-carboxylic acid or its esters, anilides, amide, &c., with oxides or hydroxides of alkalis or alkaline earths. In the case of phenylglycine and its simpler derivatives, such as tolylglycine, it is also advisable to add sodium or sodamide. The addition of reducing agents, such as iron, sulphites, or sodium ethoxide, also improves the yield. The temperature should not rise above 300°, so that no distillation occurs. After dissolving in water, the indoxyl derivatives simultaneously formed are removed by oxidation, and the indole is extracted from the filtrate by means of ether or benzene, or by distillation with steam, and finally precipitating as picrate.

C. H. D.

Colouring Matters derived from Pyridine. II. W. KÖNIG (*J. pr. Chem.*, 1904, [ii], 70, 19—56. Compare this vol., i, 449; Zincke, this vol., i, 448).—The occurrence in two modifications and the

fluorescence of the colouring matters derived from pyridine by the action of the cyanogen bromide and a primary aromatic amine are now ascribed to desmotropism between the forms $\begin{matrix} CH{:}CH{\cdot}CH{:}NR \\ | \\ CH{:}CH{\cdot}NH_2RX \end{matrix}$ and $\begin{matrix} CH{:}CH{\cdot}CH{\cdot}NHR \\ | \quad\quad\quad | \\ CH{:}CH{\cdot}NHRX \end{matrix}$. The first is the hydrohaloid of a dianilide of glutaconic aldehyde, the second is an arylaminoaryldihydropyridinium haloid.

The following compounds are described, the temperatures indicated being melting points.

Arylaminoaryldihydropyridinium Bromides.—From *p*-nitroaniline, $R = C_6H_4{\cdot}NO_2$, 149°; from *m*-nitroaniline, 167°; from *o*-toluidine, $R = C_6H_4Me$, 165°; from *m*-toluidine, 143°; from *p*-toluidine, 166°; from *o*-anisidine, $R = C_6H_4{\cdot}OMe$, 148°; from *p*-anisidine, 148—149°; from *p*-aminodimethylaniline, $R = C_6H_4{\cdot}NMe_2$, 175°.

Of the nitroanilines, the para-compound combines most readily with pyridine and cyanogen bromide, forming the colouring matter, whilst this reaction takes place least readily with the ortho-isomeride; the product from the latter has not been purified.

Arylpyridinium salts, $CH{<}^{CH\cdot CH}_{CH:CH}{>}NRCl$, are obtained when the foregoing colouring matters are heated with hydrochloric acid at 140° or boiled with naphthalene or nitrobenzene. The colouring matters from the toluidines are decomposed when boiled with toluidine, whereas that from *p*-aminodimethylaniline yields the arylpyridinium bromide when boiled with chloroform.

The following arylpyridinium salts were prepared: From *p*-nitroaniline, $R = C_6H_4{\cdot}NO_2$: *ferrichloride*, 141°; *aurichloride*, 269°; *platinichloride*, 231° (with decomposition); *ferrichloride* of the *bromide*, 149°. From *m*-nitroaniline: *bromide*, 229—230°; *ferrichloride* of the *bromide*, 163°; *picrate*, 135°; *dichromate*, 206° (with decomposition); *platinichloride*, 236°; *aurichloride*, 233°. From *o*-toluidine, $R = C_6H_4Me$: *ferrichloride* of the *bromide*, 105°; *platinichloride*, decomposes at 219°; *picrate*, 132°. From *m*-toluidine: *ferrichloride* of the *bromide*, 101°; *aurichloride*, 176°. From *p*-toluidine: *ferrichloride* of the *bromide*, 151—152°. From *p*-anisidine, $R = C_6H_4{\cdot}OMe$: *ferrichloride* of the *bromide*, 164°. From *p*-aminodimethylaniline, $R = C_6H_4{\cdot}NMe_2$: *dipicrate*, 139—140°.

The action of hydrochloric acid on the colouring matter from *p*-nitroaniline at 180° leads to the formation of 2 : 3 : 5 : 6-tetrachloroquinol. When acted on by bromine in boiling glacial acetic acid solution, the colouring matter from *p*-nitroaniline yields 2 : 6-*dibromo*-p-*nitrophenylpyridinium perbromide*, $C_6H_2Br_2(NO_2){\cdot}C_5H_5NBr_3$, which crystallises in yellow plates and melts at 217—218°, and 2 : 6-dibromo-*p*-nitroaniline. 2 : 6-*Dibromo*-p-*nitrophenylpyridinium bromide*, obtained from the perbromide by the action of boiling acetone or acetic acid, crystallises in yellow plates and melts at 280°.

The action of sodium hydroxide on *p*-nitrophenylpyridinium chloride and on 2 : 6-dibromo-*p*-nitrophenylpyridinium bromide leads to the formation of red *compounds*, of which that derived from the dibromo-

compound crystallises in microscopic needles and melts at 165—166°. To these substances, which are analogous to those described by Zincke, the following desmotropic formulæ are ascribed :

$$\begin{array}{l} CH{:}CH{\cdot}CH{:}NR \\ | \\ CH{:}CH{\cdot}OH \end{array} \quad \text{and} \quad \begin{array}{l} CH{:}CH{\cdot}CH{\cdot}NHR \\ | \qquad\quad | \\ CH{:}CH{\cdot}O \end{array} ,$$

where R is $C_6H_4{\cdot}NO_2$ or $C_6H_2Br_2{\cdot}NO_2$.

The supposed formation of a colouring matter from *o*-toluidine and 2-methylpyridine is found to have been due to the presence of pyridine. On the other hand, a colouring matter is formed with 3-methylpyridine. G. Y.

Influence of Oxides and Salts of Rare Elements on Skraup's Quinoline Synthesis. Benjamin M. Margosches (*J. pr. Chem.*, 1904, [ii], 70, 129—136).—The yield of quinoline in Skraup's synthesis is increased by the addition of commonly occurring metallic salts such as those of copper and iron. The condensation also takes place, but not to the same extent, if the nitrobenzene is replaced by the mixture of oxides or sulphates of the rare elements obtained from commercial cerium oxalate. G. Y.

Preparation of 2-Phenylquinoline. Ernst Murmann (*Monatsh.*, 1904, 25, 621—631. Compare Abstr., 1892, 1003).—The author describes a series of quantitative experiments in the preparation of 2-phenylquinoline from cinnamaldehyde and aniline, using sulphuric or hydrochloric acid as the condensing, nitrobenzene, picric acid, or arsenic acid as the oxidising, agent. The best yield (31 per cent. of the calculated quantity of pure 2-phenylquinoline) was obtained by mixing aniline (93 parts), nitrobenzene (9 parts), and water (12 parts), cooling, and adding sulphuric acid (120 parts), and finally introducing 33 parts of the aldehyde, the mixture being well stirred and then heated at 135—142° for five hours. The author discusses the causes of the small yields in such syntheses. G. Y.

***as*-Phenylbenzylhydrazine.** Rudolf Ofner (*Monatsh.*, 1904, 25, 593—602. Compare Philips, Abstr., 1889, 1159 ; Minunni, Abstr., 1893, i, 97).—*as*-Phenylbenzylhydrazine, freshly prepared from benzyl chloride and phenylhydrazine, contains 10—20 per cent. of phenylbenzylbenzylidenehydrazine (Philips, *loc. cit.*). The hydrazone is precipitated on adding cold alcohol, or when the hydrazine is dissolved in very dilute aqueous hydrochloric acid. If the hydrochloride of the hydrazine is precipitated by addition of concentrated hydrochloric acid and allowed to remain in contact with the mother liquor, it gradually changes into the hydrazone, the conversion being complete in 2—3 weeks. Free phenylbenzylhydrazine also changes, but more slowly, into phenylbenzylbenzylidenehydrazine ; after five years, a specimen contained 45 per cent. of the latter substance. The change is accompanied by the formation of phenylhydrazine.

as-Phenylbenzylhydrazine, which has been rapidly purified by solution in very dilute hydrochloric acid, precipitation of the hydrochloride, and liberation of the base, is a colourless oil which boils at 216—218° under 38 mm. pressure. With benzylaniline, phenylbenzylhydrazine forms phenylbenzylbenzylidenehydrazine and aniline,

Minunni's supposed semicarbazide of phenylbenzylhydrazine was the benzylidenehydrazine, as also was Philips' diphenyldibenzyltetrazone.

Paal and Bodewig's bisphenyl-*o*-nitrobenzylhydrazine (Abstr., 1892, 1455) was probably phenyl-*o*-nitrobenzyl-*o*-nitrobenzylidenehydrazine.

G. Y.

Quinine Glycerophosphates. P. CARRÉ (*Bull. Soc. chim.*, 1904, [iii], 31, 803—805).—When glyceryl dihydrogen phosphate (this vol., i, 133, 215) (1 mol.), dissolved in alcohol, is mixed with quinine (2 mols.) dissolved in the same solvent, the salt,

$$C_3H_5(OH)_2\cdot O\cdot PO(OH)_2(C_{20}H_{24}O_2N_2)_2,$$

is formed and may be obtained in colourless needles by addition of ether (compare Adrian and Trillat, Abstr., 1898, i, 550). The salt is slightly soluble in water; the anhydrous form melts at 148·5° and is soluble in acetone, whereas the tetrahydrate begins to melt at 147·5° and is insoluble in acetone.

The salt, $C_3H_5(OH)_2\cdot O\cdot PO(OH)_2,C_{20}H_{24}O_2N_2$, similarly prepared, forms white needles, melts at 151—152°, and has solubilities similar to those of the preceding salt, the dihydrate being insoluble in acetone.

T. A. H.

Preparation of Hydroxyhydroquinine. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 152174).—On dissolving quinine or its salts in cold concentrated sulphuric acid and diluting with water until the solution contains 20 per cent. of sulphuric acid and boiling, the soluble sulphonic acid at first formed is converted into hydroxyhydroquinine. Sodium hydroxide precipitates the base, which forms a bitter, white, crystalline powder, dissolving very sparingly in water or ether, readily in alcohol or acetone. The hydrochloride forms crystals containing $2H_2O$, becomes anhydrous at 100°, and darkens at 175°.

C. H. D.

Pyrimidines. Synthesis of 2-Amino-5-methyl-6-oxypyrimidine. TREAT B. JOHNSON and SAMUEL H. CLAPP (*Amer. Chem. J.*, 1904, 32, 130—145).—2-*Amino-6-oxy-5-methylpyrimidine*,

$$NH{<}{\substack{C(NH_2){:}N \\ CO—CMe}}{>}CH,$$

obtained by the condensation of guanidine with ethyl sodioformylpropionate, crystallises in prisms, melts and decomposes at 320—321°, and is soluble in water at 25° to the extent of 0·43 per cent.; it dissolves readily in sodium hydroxide solution, and is reprecipitated on neutralisation with carbon dioxide or dilute sulphuric acid. The *hydrochloride*, *picrate*, *sulphate*, and *platinichloride* are described.

α-Methyl-β-guanidineacrylic acid, formed as an intermediate product in the preparation of 2-amino-6-oxy-5-methylpyrimidine, is capable of existing in two modifications. trans-α-*Methyl-β-guanidineacrylic acid*, $\begin{matrix} CH_3\cdot C\cdot CO_2H \\ \Vert \\ (NH_2)_2C{:}N\cdot CH \end{matrix}$, crystallises in prisms, melts and decomposes at 329—332°, is soluble in water at 25° to the extent of 0·08 per cent., and has both basic and acidic properties. When this acid is dissolved in 9 per cent. sodium hydroxide solution, it is converted into

2-amino-6-oxy-5-methylpyrimidine, but cold sodium hydroxide of 2 per cent. strength does not effect this change. cis-*a-Methyl-β-guanidine-acrylic acid*, $\begin{matrix}CH_3\cdot C\cdot CO_2H \\ \Vert \\ HC\cdot N\colon C(NH_2)_2\end{matrix}$, crystallises in slender needles, melts at 319—320°, slowly decomposes at a higher temperature, and has a solubility in water at 25° of 0·84 per cent. This modification, unlike the *trans*-acid, cannot be reprecipitated from an alkaline solution, but is converted into the pyrimidine even by cold 2 per cent. sodium hydroxide.

By the condensation of ethyl formate with ethyl phthaliminoacetate in presence of sodium, ethyl sodioformylphthaliminoacetate is obtained. When a solution of this compound is acidified with hydrochloric acid, ethyl 4-hydroxy*iso*carbostyril-3-carboxylate (Gabriel and Colman, Abstr., 1900, i, 358) is produced. 5-*Phthalimino-2-ethylthiol-6-oxypyrimidine*, $NH<\begin{matrix}C(SEt)=\!=\!=\!=N \\ CO\cdot(N\colon C_8H_4O_2)C\end{matrix}>CH$, prepared by the condensation of ψ-ethylthiocarbamide with ethyl sodioformylphthaliminoacetate, crystallises in rhombic plates and melts at 230—231°; when dilute hydrochloric or sulphuric acid is added to a solution of this compound in an alkali hydroxide, *a-phthalimino-β-ψ-ethylthiocarbamidoacrylic acid*, $NH_2\cdot C(SEt)\colon N\cdot CH\colon C(N\colon C_8H_4O_2)\cdot CO_2H$, is precipitated, which crystallises from alcohol in small prisms, melts at 131°, and is decomposed at a higher temperature with formation of the pyrimidine.

5-*Benzoylamino-2-ethylthiol-6-oxypyrimidine*,

$$NH<\begin{matrix}C(SEt)=\!=N \\ CO\cdot C(NHBz)\end{matrix}>CH,$$

obtained by the action of ψ-ethylthiocarbamide on ethyl sodium hydroxymethylenehippurate, crystallises from alcohol in needles and melts at 238—239°; it is soluble in alkali hydroxides and is reprecipitated by hydrochloric acid. E. G.

Uric Acid Group. Constitution of Murexide and of Several of the Derivatives of Uric Acid related to it. By Oscar Piloty and Karl Finckh (*Annalen*, 1900, 333, 22—71).—After a summary of the present view of the constitution of murexide, new methods of preparing this substance are described.

A solution of alloxantin (5 grams) in 200 c.c. of boiling water is poured into a solution of ammonium acetate (25 grams) in 100 c.c. of water at 80°, just alkaline with ammonia; murexide in a yield of 80 per cent. crystallises out; a small quantity of uramil separates afterwards. Excess of ammonia must be avoided, and the ammonium acetate cannot be replaced by another ammonium salt with advantage. The alloxantin may, however, be replaced by a mixture of ammonium dialurate and alloxan. These reactions account for the formation of murexide from uric acid and nitric acid and for the ordinary murexide test for uric acid, in both cases alloxantin being formed as an intermediate product.

Potassium purpurate can be very readily prepared by shaking up a solution of potassium uramil with an ethereal solution of iodine, the purpurate crystallising out during the process: $2C_4H_3O_3N_3K_2 + 2I +$

$H_2O = C_4H_4O_3N_5K + 2KI + KOH + NH_3$. In the presence of the excess of alkali, a portion of the uramil is oxidised to oxalic acid.

In agreement with Beilstein (*Annalen*, 1858, 107, 176), murexide is found to have the composition $C_8H_8O_6N_3,H_2O$, the water of crystallisation being lost at 110°. In addition to the sodium salts previously described by Fritzsche (*Annalen*, 1839, 32, 316), a *sodium* salt,

$$C_8H_7O_6N_3Na,H_2O,$$

isomeric with Fritzsche's salt, was obtained by adding a saturated solution of sodium hydrogen carbonate to a solution of that salt, and forms slender, grass-green needles; when a solution of this salt is added to a little warm dilute sodium hydroxide, another *sodium* salt, $C_8H_3O_6N_5Na_2,3H_2O$, crystallises out in bright red needles.

The decomposition of murexide by acids yields alloxantin, uramil, and alloxan in varying proportions, as Liebig and Wöhler found; it is suggested that alloxantin is the primary product, which (as has been shown above) reacts with the ammonium chloride formed to give uramil and alloxan.

Since neither the degradation of murexide nor its synthetic formation from uramil and alloxan can be carried out in such a way as to throw light on its constitution, it was hoped to gain some information in the preparation of murexide-like substances from alloxan. A series of dyes has thus been synthesised; they are called the "ureïdes."

Dimethylureideindoaniline, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C:N\cdot C_6H_4\cdot NMe_2$, is prepared by mixing in alcoholic solution alloxan (1 mol.) and *as*-dimethyl-*p*-phenylenediamine (1 mol.), when small, dark blue crystals with a green reflex separate; it decomposes on heating, and is immediately converted by acids (even acetic acid) into alloxan and the diamine, and is reduced to a colourless base which is oxidised by the air in the presence of alkalis. *Tetramethylureideindoaniline*, prepared from 1 : 3-dimethylalloxan and *as*-dimethyl-*p*-phenylenediamine, the two substances being mixed in chloroform solution, forms blue prisms with a green reflex and melts at 168°; it is immediately decomposed into its components by acids and alkalis, and is reduced by zinc dust and acetic acid to a colourless, amorphous base, the *platinichloride* of which has been obtained as orange-yellow needles. In a similar manner, *p*-aminophenol can be substituted for the diamine, ureideindophenols being formed; similar substances are produced when dimethyl- or dibromoalloxan is used. The constitution represented by the above formula is assigned to these compounds from the analogy which they show both in method of formation and properties to phenylindophenol,

$$CO<\begin{matrix}CH:CH\\CH:CH\end{matrix}>C:N\cdot C_6H_4\cdot NMe_2,$$

which is produced by condensation of quinone and *as*-dimethyl-*p*-phenylenediamine, is immediately decomposed into its components by acids, and is insoluble in alkali hydroxides. It is suggested that in this condensation alloxan behaves as if it had a quinonoid structure.

Since quinoneoxime, that is, nitrosophenol, condenses with phenols, it was thought that the similarly constituted alloxan derivative,

violuric acid, would be capable of a similar reaction; violuric acid will not react with phenols, but condenses with *m*-phenylenediamine, forming *ureideaminoazine*,

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C{:}N\cdot C\leqslant\begin{matrix}CH{=\!=\!=}CH\\C(NH_2)\cdot CH\end{matrix}\geqslant C\cdot NH_2;$$

this substance is prepared by adding a solution of sodium hydroxide to a mixture of violuric acid and *m*-phenylenediamine hydrochloride, and separates as a brick-red, insoluble crystalline powder, which dissolves in sodium hydroxide, being converted into the *sodium* salt, $C_{10}H_6O_2N_5Na,\frac{1}{2}H_2O$, which forms slender, golden-yellow needles. Dimethylvioluric acid and *m*-phenylenediamine produce the *compound* $C_{10}H_5O_2N_5Me_2$, which can be crystallised from concentrated hydrochloric acid in yellow needles, soluble in sulphuric acid with a cherry-red coloration, and decomposing on heating. From these observations, the inference is drawn that violuric acid is the oxime of a substance of a quinonoid nature.

Alloxan and 1-amino-2 : 4-dihydroxybenzene condense to form the ureideoxazones, the alloxan again behaving as a quinone, thus, dimethylalloxan and aminoresorcinol, when mixed in alcoholic solution, yield a *compound*, $C_{12}H_{11}O_5N_3,H_2O$, which forms a reddish-brown powder decomposing at a high temperature, and can be boiled with acids; the solutions of the salts are dark blue, the solution in sulphuric acid has the colour of permanganate. *Ureidehydroxyoxazone*, prepared from alloxan and aminoresorcinol, was isolated in the form of the *barium* salt, $C_{10}H_6O_5N_3Ba,2H_2O$, which is an amorphous, dark blue precipitate. The great stability of these ureidehydroxyoxazones offers a marked contrast to the ureideindophenyl compounds; further, a comparison of the properties of this class with those of the hydroxydinaphtha-oxazones points to a close resemblance between the constitution of these two classes of substances; the formula

$$OH\cdot C_6H_3<\begin{matrix}N{:}C\cdot CO-NMe\\O\cdot C(OH)\cdot NMe\end{matrix}>CO,$$

resembling that of the naphtha-oxazone, is therefore suggested.

From the results above described, it might be concluded that murexide was a ureideindophenol, thus:

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C{:}N\cdot C<\begin{matrix}CO{-\!-\!-\!-}NH\\C(O\cdot NH_4)\cdot NH\end{matrix}>CO,$$

but the stability of murexide and the ease of its formation are opposed to this view; it seems more probable that it is a ureidehydroxyoxazone,

$$\begin{matrix}NH\cdot CO\cdot C{=\!=\!=\!=\!=\!=}N\cdot C\cdot CO\cdot NH\\ |\qquad\quad |\qquad\qquad\qquad |\qquad\; |\\ CO\cdot NH\cdot C(O\cdot NH_4)\cdot O\cdot C\cdot NH\cdot CO\end{matrix},$$

a constitution which would account for its formation from uramil and alloxan and for its decomposition into alloxan, dialuric acid, and ammonia on the one hand (the alloxan and dialuric acid recombine to form the alloxantin), and into alloxan, uramil, and ammonia on the other; thus, $C_8H_8O_6N_3 + 2H_2O + 2HCl = C_4H_2O_4N_2 + C_4H_2O_2N_2(OH)_2 + 2NH_4Cl$ and $C_8H_8O_6N_3 + H_2O + HCl = C_4H_2O_4N_2 + C_4H_2O_2N_2(OH)\cdot NH_2 + NH_4Cl$. The want of stability of murexide towards acids is a difficulty in the way of this view, but it is pointed out that the benzene ring confers stability on the oxazone ring, and that in murexide this ring is linked with a ureide ring, a

fact which probably accounts for the instability towards acids. For murexide is suggested the name *ammonium diureideoxazonate.*

A consideration of the properties of alloxantin shows that the formula at present accepted, $\left[CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C(OH)\cdot\right]_2$, is unsatisfactory; for example, alloxantin does not form stable salts, and is decomposed by dilute and cold solutions of alkalis into salts of alloxan and dialuric acid, the same decomposition being even effected by ammonium chloride and dimethylamine acetate; moreover, hydroxylamine converts this substance into the oxime of alloxan, violuric acid; a mixture of mol. quantities of alloxan and ammonium dialurate, which in these circumstances yields no alloxantin, produces as much murexide as the equivalent quantity of alloxantin. It appears, therefore, as if the components of alloxantin, dialuric acid, and alloxan were already present in very loose combination. This relation is best expressed by supposing that alloxantin bears to alloxan the relation that quinhydrone bears to quinone, thus:

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C(OH)\cdot O\cdot C<\begin{matrix}C(OH)\cdot NH\\CO\text{——}NH\end{matrix}>CO\,;$$

a comparison of the properties of quinhydrone and alloxantin confirms this view, and, further, a comparison of the properties of alloxan and quinone shows that they have a similar chemical behaviour; they act as oxidising agents, yield dyes, colour the skin, combine, on the one hand, with dialuric acid, and, on the other hand, with quinol, producing similar substances, alloxantin and quinhydrone, and are reduced respectively by hydrochloric and hydrobromic acids to alloxantin and quinhydrone.

When alloxantin in aqueous solution is treated with excess of a methylamine acetate solution, 7-methyluramil crystallises from the deep violet solution. 7-*Ethyluramil*, $C_4H_4O_3N_3Et$, is formed when ethylamine is substituted for methylamine, and crystallises in lustrous plates or slender needles. With dimethylamine, the coloration produced is not so marked, and no compound could be isolated on concentration.

7-Ethyluramil and alloxan react in the presence of ammonium carbonate, giving a deep purple-red solution from which murexide separates.

Alloxan and methyl- and ethyl-amines yield deeply-coloured solutions from which the corresponding purpurates of methylamine and ethylamine separate; a substituted murexide is not produced. When glycine is used instead of the base, a deeply-coloured solution is obtained from which the *glycine* salt of purpuric acid,

$$C_{10}H_{10}O_8N_6,2H_2O,$$

crystallises out in dark red, prismatic leaflets with a green reflex; it is decomposed by water and converted by treatment with a solution of ammonium chloride into murexide, glycine hydrochloride being at the same time formed. If the glycine and the alloxan are allowed to react at a higher temperature, the purpurate first formed is decomposed, and an amorphous substance, which is soluble in alkalis, is produced together with a *compound*, $C_6H_7O_5N_3,H_2O$; the latter crystallises in yellow needles, gives a blue alloxan reaction with ferrous sulphate, and is possibly uramilacetic acid.

K. J. P. O.

Preparation of 3′ : 8-Dichlorocaffeine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 151190. Compare D.R.-P. 105050).—3′ : 8-Dichlorocaffeine is most readily prepared by passing a rapid stream of chlorine into fused 8-chlorocaffeine at 200°, the temperature being gradually lowered to 170°. At 150—160°, some 7′ : 8-dichlorocaffeine is also produced.
C. H. D.

Action of Hydroxylamine and of Hydrazine on β-Alkyloxy- and β-Phenoxy-ethylenic Ketones. CHARLES MOUREU and M. BRACHIN (*Compt. rend.*, 1904, 139, 294—297).—The β-alkyloxy- and β-phenoxy-ethylenic ketones, OR″·CR:CH·COR′ (compare this vol., i, 811), react with hydroxylamine to form *iso*oxazoles identical with those obtained by the action of hydroxylamine on the acetylenic ketones (compare this vol., i, 95), thus, 5-phenyl-3-ethyl*iso*oxazole was obtained from β-propionyl-α-ethoxystyrene, and 5-phenyl-3-propyl*iso*oxazole from β-butyryl-α-phenoxystyrene. The reaction probably takes place in two stages: (1) the formation of the oxime, OR″·CR:CH·CR′:NOH; (2) the elimination of one mol. of alcohol or phenol to form the *iso*oxazole, $O<\begin{matrix}N=CR'\\CR:CH\end{matrix}$. By a similar reaction, β-alkyloxy- and β-phenoxy-ethylenic ketones yield pyrazoles on treatment with hydrazine, identical with those obtained by the action of hydrazine on the corresponding acetylenic ketones (compare Abstr., 1903, i, 581). 5-*Phenyl-3-ethylpyrazole*, $NH<\begin{matrix}N=CEt\\CPh:CH\end{matrix}$, boils at 205—207° (corr.) under 17 mm. pressure, crystallises from light petroleum in colourless prisms melting at 82°, and forms a *picrate* crystallising in thin, prismatic needles, melting at 146°, on Maquenne's metal block. 5-*Phenyl-3-propylpyrazole*, $NH<\begin{matrix}N=CPr\\CPh:CH\end{matrix}$, boils at 212—215° under 20 mm. pressure and melts at 68°, its *picrate* crystallises in rhomboidal plates and melts at 105° on Maquenne's metal block.
M. A. W.

Uramil. OSCAR PILOTY and CARL FINCKH (*Annalen*, 1904, 333, 71—99. Compare this vol., i, 820).—Uramil is very simply prepared by heating ammonium dialurate, closed vessels being employed to avoid oxidation.

Potassium uramil, $CO<\begin{matrix}NK\cdot CO\\NK\cdot CO\end{matrix}>CH\cdot NH_2,2H_2O$, is obtained as slender, pale yellow needles by dissolving uramil in 50 per cent. warm potassium hydroxide, when partial decomposition takes place; the salt cannot be recrystallised without loss of potassium, and when exposed to moist air becomes intensely red, ammonia being evolved. Iodine converts the salt into potassium murexide, methyl iodide into 1 : 3-dimethyluramil (Techow, Abstr., 1895, i, 83). Of the salts of the form, $CO<\begin{matrix}NH\cdot CO\\NM:CO\end{matrix}>CH\cdot NH_2$, only the *barium* and *lead* salts have been prepared; the former is obtained by adding barium chloride to a solution of uramil in ammonia, and the latter as needles which readily become

rose-coloured in the air. The *acid potassium* salt, $C_4H_5O_3N_3,C_4H_4O_3N_3K$, is prepared by dissolving uramil in boiling dilute potassium hydroxide and crystallises in colourless, sparsely soluble leaflets which rapidly become red in the air; the sodium salt closely resembles the potassium salt.

When boiled with ten per cent. alkali hydroxide for several hours, uramil is decomposed, carbamide and aminomalonic acid being formed; further, the carbamide combines with the unchanged uramil, forming ψ-uric acid, with the elimination of ammonia,

$$CO<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}>CH\cdot NH\cdot CO\cdot NH_2.$$

The ψ-uric acid is in its turn hydrolysed into carbamide and *carbamidomalonic acid*, $NH_2\cdot CO\cdot NH\cdot CH(CO_2H)_2$. From the product of the reaction, *potassium ψ-urate*, $C_5H_5O_4N_4K,H_2O$, crystallises; the filtrate is evaporated and alcohol added, when the potassium salts of aminomalonic and carbamidomalonic acids separate as an oil, from which the potassium aminomalonate slowly crystallises. The carbamidomalonic acid is purified by converting the oily potassium salt into the lead salt, from which the free acid can be prepared; it forms prisms melting and decomposing at 148—150°; it is decomposed by boiling with water, hydantoic acid (melting and decomposing at 155°) being formed; the *potassium* salt is extremely soluble, the *ammonium* salt, $C_4H_4O_5N_2(NH_4)_2,H_2O$, crystallises in soluble needles, the *barium* salt crystallises in lustrous prisms with $2H_2O$, and the *lead* salt with H_2O in prisms, and the *silver* salt in anhydrous prisms.

It has been ascertained that the "uramilic acid," $C_{16}H_{20}O_{15}N_{10}$, described by Liebig and Wöhler (*Annalen*, 1838, 26, 314) as being formed by the action of dilute sulphuric acid on uramil, is the *acid ammonium* salt of hydurilic acid (Schlieper, *Annalen*, 1845, 56, 11; and Bayer, *ibid.*, 1864, 132, 302).

7-Acetyluramil, which can be easily purified by conversion into the ammonium salt, is hydrolysed by boiling with water and forms a series of salts; the *potassium* salt, $C_6H_6O_4N_3K$, crystallises in rhombic prisms, and the *ammonium* and *silver* salts in slender needles; the *barium, lead*, and *copper* salts are all crystalline.

When dipotassium uramil is oxidised in aqueous solution in the cold, a crystalline *potassium* salt, $C_4H_4O_4N_3K,\frac{1}{2}H_2O$, can be isolated; on acidifying this salt, carbon dioxide is evolved, and acid potassium alloxanate can be isolated from the product. On treating the alkaline solution of the salt, ammonia is evolved and normal potassium alloxanate formed. The potassium salt is isomeric with potassium oxonate, obtained by oxidising uric acid (Medicus, *Annalen*, 1875, 175, 232). It is suggested that this new acid is *aminohydantoincarboxylic acid*, $CO<\begin{matrix}NH\cdot CO\\ \quad\ \ |\\ NH\cdot C(NH_2)\cdot CO_2H\end{matrix}$. Attempts to obtain a simila- compound by oxidising ψ-uric acid led only to the formation of alloxanic acid.

When alloxan is treated in aqueous solution with a neutral solution of dimethylamine sulphite, the expected dimethylamine dimethylthionurate is not formed, but the *dimethylamine* salt,

$$CO<\begin{matrix}NH\text{———}CO\\ N(NHMe_2)\cdot CO\end{matrix}>C(OH)\cdot SO_3\cdot NH_2Me_2,$$

which is obtained as needles or prismatic crystals on evaporating the product of the reaction; exposed to the air, the compound becomes rose-coloured, and when heated at 120° dimethylamine is given off and the substance assumes the colour of murexide. When the solution is boiled, it becomes pale red, but little decomposition occurs; on heating the concentrated aqueous solution under pressure at 140°, complete decomposition takes place, carbon dioxide, sulphur dioxide, ammonia, dimethylamine, and sulphuric acid being produced. When warmed with dilute acids, sulphur dioxide is evolved and alloxantin and dimethylamine produced; no trace of substituted uramil was discovered.

The *potassium* salt, $C_4H_2O_7N_2SK_2,H_2O$, prepared from the dimethylamine salt, crystallises in prisms, and the *ammonium* salt, which is anhydrous, in sparingly soluble plates; the *barium* salt crystallises in needles with $2H_2O$, and the *lead* salt in nodular aggregates.

The constitution of the sulphite additive compounds of alloxan is discussed in the light of these results, and it is concluded that thionuric acid must be represented by the formula

$$CO{<}{\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}}{>}CH\cdot NH\cdot SO_3H.$$

K. J. P. O.

Action of Carbimides and Thiocarbimides on Hydrazo-acids. James R. Bailey (*J. Amer. Chem. Soc.*, 1904, 26, 1006—1026). —[With Salomon F. Acree and P. T. Miller.]—1-*Carbamido-3-phenyl-5-methyl-2-thiohydantoin*, $NH_2\cdot CO\cdot NH\cdot N{<}{\begin{matrix}CHMe\cdot CO\\ CS\text{——}NPh\end{matrix}}$, prepared by boiling an alcoholic mixture of phenylthiocarbimide and ethyl semicarbazinopropionate for half an hour, crystallises from methyl alcohol in aggregates of short, colourless prisms and melts and decomposes at 206°. The analogous 1-*carbamido-5-methyl-3-allyl-2-thiohydantoin*, prepared by using allylthiocarbimide, melts at 167°. 1-*Carbamido-5-methyl-3-ethyl-2-thiohydantoin* crystallises from alcohol and melts at 153°.

1-*Carbamido-3-phenyl-5-dimethyl-2-thiohydantoin*,

$$NH_2\cdot CO\cdot NH\cdot N{<}{\begin{matrix}CMe_2\cdot CO\\ CS\text{——}NPh\end{matrix}},$$

obtained by boiling a solution of ethyl semicarbazino*iso*butyrate and phenylthiocarbimide in ethyl acetate, decomposes at 191°.

1-*Amino-3-phenyl-5-methyl-2-thiohydantoin*, prepared by heating 1-carbamido-3-phenyl-5-methyl-2-thiohydantoin with concentrated hydrochloric acid for 1 hour at 120°, crystallises from water or alcohol in long, slender, pointed prisms, melts at 150°, and combines with phenylthiocarbimide to form a *thiocarbamide* decomposing at 223°. 1-*Amino-3-phenyl-5-dimethyl-2-thiohydantoin*, prepared similarly, crystallises from alcohol in long needles, melts at 173°, and with a boiling acetic acid solution of phenylthiocarbimide gives the crystalline *derivative*, $C_{18}H_{13}ON_4S_2$, which decomposes at 233°; the *benzylidene* derivative, $C_{18}H_{17}ON_3S$, of the amino-compound crystallises from alcohol and melts at 135°.

When 1-carbamido-3-phenyl-5-methyl-2-thiohydantoin is heated with aqueous barium hydroxide at 65°, it is probably first hydrolysed to the compound $NH_2\cdot CO\cdot NH\cdot N(CHMe\cdot CO_2H)\cdot C(SH)\colon NPh$, which, by loss of NH_3, gives 2-*phenylimino*-5-*hydroxy*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*-3-*propionic acid*, $CO_2H\cdot CHMe\cdot N{<}\begin{matrix}C(NPh)\cdot S\\ N{=\!=\!=}C\cdot OH\end{matrix}$; this crystallises from water in clusters of radiating needles, melts and decomposes at 220°, and can be titrated with sodium hydroxide as a dibasic acid; its *ethyl* ester $C_{13}H_{15}O_3N_3S$, crystallises from alcohol or benzene, melts at 171°, and gives a *benzoyl* derivative, $C_{20}H_{19}O_4N_3S$, crystallising in thin plates and melting at 110°. The *amide*, $C_{11}H_{12}O_2N_4S$, of the acid, crystallises from alcohol and melts and decomposes at 228°.

1-*Carboxy*iso*propylamino*-3-*phenyl*-5 : 5-*dimethyl*-2-*thiohydantoin*,

$$CO_2H\cdot CMe_2\cdot NH\cdot N{<}\begin{matrix}CMe_2\cdot CO\\ CS\text{——}NPh\end{matrix},$$

prepared by heating hydrazo*iso*butyric acid and phenylthiocarbimide with boiling glacial acetic acid, crystallises from benzene and ether, melts at 153°, and is hydrolysed by hydrochloric acid at 140—160°, giving 1-amino-3-phenyl-5 : 5-dimethyl-2-thiohydantoin (*supra*), a fact which confirms its structure. The *nitroso*-derivative, $C_{15}H_{18}O_4N_4S$, of the foregoing amino-compound crystallises from a mixture of benzene and light petroleum and melts and decomposes at 166°. The *methyl* ester, $C_{16}H_{21}O_3N_3S$, melts at 142°; the *ethyl* ester, $C_{17}H_{23}O_3N_3S$, melts at 84°.

1-*Carboxy*iso*propylamino*-5 : 5-*dimethyl*-3-*allyl*-2-*thiohydantoin* crystallises from benzene and melts at 121°; the analogous 3-*ethyl* derivative melts at 110°, and the 3-*methyl* compound at 129°. 1-*Phenylamino*-3-*phenyl*-5 : 5-*dimethyl*-2-*thiohydantoin*, $NHPh\cdot N{<}\begin{matrix}CMe_2\cdot CO\\ CS\text{——}NPh\end{matrix}$, prepared from phenylhydrazo*iso*butyric acid and phenylthiocarbimide, crystallises from benzene and melts at 206°. 1-*Phenylamino*-5 : 5-*dimethyl*-3-*ethyl*-2-*thiohydantoin*, obtained by using ethylthiocarbimide, melts at 85°.

α-*Carbamido*-αβ-*diphenylcarbamide*, $NHPh\cdot CO\cdot NPh\cdot NH\cdot CO\cdot NH_2$, prepared by boiling a benzene solution of phenylsemicarbazide and phenylcarbimide, crystallises from alcohol and melts and decomposes at 210°. When phenylcarbimide is boiled in benzene solution with ethyl semicarbazinopropionate, the *additive compound*,

$$NH_2\cdot CO\cdot NH\cdot N(CO\cdot NHPh)\cdot CHMe\cdot CO_2Et,$$

melting at 163°, is obtained. On boiling this with water, 1-*carbamino*-3-*phenyl*-5-*methylhydantoin*, $NH_2\cdot CO\cdot NH\cdot N{<}\begin{matrix}CHMe\cdot CO\\ CO\text{——}NPh\end{matrix}$, is formed; it crystallises from ethyl acetate in long, slender needles and melts and decomposes at 219°.

1-*Carboxy*iso*propylamino*-3-*phenyl*-5 : 5-*dimethylhydantoin*,

$$CO_2H\cdot CMe_2\cdot NH\cdot N{<}\begin{matrix}CMe_2\cdot CO\\ CO\text{——}NPh\end{matrix},$$

obtained by desulphurising the corresponding thiohydantoin with mercuric oxide or by the action of phenylcarbimide on hydrazo*iso*butyric acid, crystallises from alcohol in characteristic prisms, melts

at 205°, and can be titrated as a monobasic acid; the *ethyl* ester crystallises from ether in large, hexagonal prisms and melts at 98°. 1-*Carboxy*iso*propylamino*-3 : 5 : 5-*trimethylhydantoin*, prepared from the corresponding thio-compound, crystallises from water in slender prisms and melts at 169°. 1-*Carboxy*iso*propylamino*-5 : 5-*dimethyl*-3-*ethylhydantoin* melts at 140°. The corresponding 3-*allyl*-derivative melts at 114°.

1-*Azo*-5 : 5-*dimethyl*-3-*ethylhydantoin*,

$$\begin{matrix} CO\cdot CMe_2 \\ | \\ NEt-CO \end{matrix}\!\!>N\cdot N:N\cdot N<\!\!\begin{matrix} CMe_2\cdot CO \\ | \\ CO-NEt \end{matrix},$$

obtained by the action of bromine water on 1-carboxy*iso*propylamino-5 : 5-dimethyl-3-ethylhydantoin in alcoholic solution, crystallises from alcohol and melts and decomposes at 234°. 1-*Azo*-3 : 5 : 5-*trimethylhydantoin* decomposes at 278° and 1-*azo*-3-*phenyl*-5 : 5-*dimethylhydantoin* at 270°. W. A. D.

1 : 2 : 3-Thiodiazoles. LUDWIG WOLFF [with H. KOPITZSCH and A. HALL] (*Annalen*, 1904, 333, 1—21. Compare Abstr., 1903, i, 203).—The cyclic diazoanhydrides, $\begin{matrix} CR:CR' \\ | \\ N=\!=\!=N \end{matrix}\!\!>O$, are converted by treatment with ammonium sulphide into thiodiazoles, $\begin{matrix} CR:CR' \\ | \\ N=\!=\!=N \end{matrix}\!\!>S$, which are more stable than the compounds from which they are produced, not being attacked by mineral acids, and only slowly decomposed by boiling alcoholic alkali hydroxides; the substituted thiodiazoles are still more stable towards alkalis. They are very feeble bases, and their hydrochlorides yield double salts with mercury, gold, and silver salts. They combine with methyl iodide, and the resulting compounds yield strong bases on treatment with silver hydroxide.

The thiodiazoles are prepared by passing a current of hydrogen sulphide through an alcoholic solution of the diazoanhydride containing a small quantity of ammonium sulphide for 20—24 hours at 0—5°. *Ethyl* 5-*phenyl*-1 : 2 : 3-*thiodiazole*-4-*carboxylate*, $\begin{matrix} C(CO_2Et):CPh \\ | \\ N=\!=\!=\!=\!=N \end{matrix}\!\!>S$, prepared from the diazoanhydride of ethyl benzoylacetate, crystallises in colourless needles or plates melting at 42°, and on hydrolysis with sodium hydroxide yields the corresponding *acid*, which crystallises in colourless needles or leaflets melting with evolution of carbon dioxide at 157°, and becomes coloured when exposed to light. *Ethyl* 5-*methyl*-1 : 2 : 3-*thiodiazole*-4-*carboxylate*, $\begin{matrix} C(CO_2Et):CMe \\ | \\ N=\!=\!=\!=\!=N \end{matrix}\!\!>S$, prepared from the diazoanhydride of ethyl acetoacetate, crystallises in needles or plates melting at 35°, and the corresponding acid (with H_2O) in needles, which melt at 74—75° and when anhydrous at 113°; it decomposes with evolution of carbon dioxide at 160°. When oxidised in alkaline solution with potassium permanganate, it is converted into 1 : 2 : 3-*thiodiazole*-4 : 5-*dicarboxylic acid*, $\begin{matrix} C(CO_2H):C(CO_2H) \\ | \\ N=\!=\!=\!=\!=\!=N \end{matrix}\!\!>S,H_2O$, which is isolated by extracting with ether and recrystallising from water containing hydrochloric

acid, when it forms colourless needles melting with evolution of carbon dioxide and formation of thiodiazole-4-carboxylic acid (m. p. 227°). The anhydrous acid melts at about 110° and is hygroscopic. This acid can also be prepared from the diazoanhydride from ethyl oxaloacetate. 1 : 2 : 3-*Thiodiazole-4-carboxylic acid*, prepared by boiling a solution of the dibasic acid just mentioned, crystallises from water, in which it is insoluble, in anhydrous prisms, decomposing at 228°.

5-*Phenyl*-1 : 2 : 3-*thiodiazole*, $\begin{matrix}CH\colon CPh \\ | \\ N = N\end{matrix}\!\!>S$, is prepared by heating small portions of the phenylthiodiazolecarboxylic acid at 160—170° and distilling the product with steam; it crystallises in prisms melting at 53—53·5°, and has an odour resembling that of nitrobenzene; this substance is very stable and is only very slowly decomposed by tin and hydrochloric acid; by a mixture of sulphuric and nitric acids, it is nitrated; the *additive* compound with mercuric chloride,

$$C_8H_6N_2S,HgCl_2,$$

crystallises in long needles, becoming coloured at 160° and melting at 167°. The *methiodide*, $C_8H_6N_2S,MeI,H_2O$, prepared by heating the base with excess of methyl iodide at 110—120° for eight hours, crystallises in pale yellow needles melting and evolving gas at 136°, then solidifying again to melt at 158°; the anhydrous substance melts at 158° and is hygroscopic; the *methochloride* forms colourless needles, and the *platinichloride* yellowish-red needles melting at 151°; the *aurichloride* crystallises in sparsely yellow prisms melting at 180°.

5-*Methyl*-1 : 2 : 3-*thiodiazole*, prepared by heating 1 : 2 : 3-methylthiodiazole-4-carboxylic acid at 185° and distilling the product under reduced pressure, is a clear liquid of pleasant odour, which does not solidify at − 18°, boils at 91° under 38 mm., at 88—89° under 34 mm., and at 184° under 755 mm. pressure; it has a sp. gr. 1·2363 at 0°, distils readily with steam, and becomes coloured when exposed to light. The *compound* with mercuric chloride crystallises in prisms; the *hydrochloride* forms hygroscopic needles, and the *aurichloride* yellow needles decomposing at 145°. The *methiodide*, $C_3H_4N_2S,MeI$, crystallises in pale yellow, hygroscopic needles melting at 76—77°; the *methochloride* forms colourless, hygroscopic needles, which yield a double *salt* with mercuric chloride, crystallising in prisms; the *platinichloride*,

$$(C_3H_4N_2S,MeCl)_2PtCl_4,$$

crystallises in orange-red needles or prisms melting and decomposing at 212°, and the *aurichloride* in yellow, lustrous leaflets melting at 136—137°. By treatment of the aqueous solution of the methiodide with moist silver oxide, a strongly alkaline solution of the free base can be prepared.

1 : 2 : 3-*Thiodiazole*, $\begin{matrix}CH\colon CH \\ | \\ N = N\end{matrix}\!\!>S$, is prepared by distilling thiodiazolecarboxylic or -dicarboxylic acid at 230—260° and distilling the resulting oil with steam; it is a clear oil with a pleasant odour, not solidifying at − 19°, and boiling at 83—85° under 60 mm. and at 157° under 742 mm. pressure; it has a sp. gr. 1·3202 at 0°, and it is very stable towards acids, although easily decomposed with evolution of nitrogen by alkali hydroxides; with silver nitrate, it gives an amorphous and

with mercuric chloride a crystalline precipitate; the *hydrochloride* crystallises in colourless, hygroscopic needles or prisms melting at 70°, and sublimable; the *salt*, $C_2H_2N_2S,AuCl_3$, crystallises in pale yellow needles which become dark at 152° and are molten at 165°; when crystallised from concentrated hydrochloric acid, the *aurichloride*, $C_2H_2N_2S,HCl,AuCl_3$, is obtained, crystallising in yellow needles decomposing at 150—160°. The *methiodide*, $C_2H_2N_2S,MeI$, is prepared in the usual manner, and crystallises in yellow prisms, which, when rapidly heated, melt and decompose at 222°, but when slowly heated become coloured at 210° and volatilise at 220°. When the aqueous solution is made alkaline, a bluish-green coloration appears, which rapidly becomes reddish-brown, nitrogen being evolved. An aqueous solution of the free base can be prepared. The *methochloride* crystallises in colourless, hygroscopic plates, decomposing into its components at 192°; the double *salt* with mercuric chloride crystallises in prisms melting at 170—171°; the *aurichloride* crystallises in yellow needles decomposing at 252°; the *platinichloride* crystallises in orange-red prisms which melt and evolve gas at 207°. K. J. P. O.

Methyl Anthranilate; its Detection of Some Derivatives. PAUL FREUNDLER (*Bull. Soc. chim.*, 1904, [iii], 31, 882—884).—*Methyl anthranilate picrate*, obtained by mixing alcoholic solutions of the two components, forms yellow needles, melts at 103·5—104°, and is readily soluble in alcohol.

When molecular quantities of methyl anthranilate and phenylthiocarbimide are warmed together at 100°, the 4-keto-2-thio-3-phenyltetrahydroquinazoline described by McCoy (Abstr., 1897, i, 490) is formed.

The latter reaction may be employed for the detection and estimation of methyl anthranilate in the absence of other esters of this acid. The ester is isolated by steam distillation in presence of sodium carbonate and extraction with ether. The oil left on distilling off the solvent is mixed with excess of phenylthiocarbimide and heated at 100—120° for 3—4 hours. The residue is then disintegrated by boiling with alcohol, and, when quite cold, the insoluble portion is filtered off and dried at 100—120°, the yield being approximately 98 per cent. of the theoretical.

The author has confirmed by this method the observation of Schmidt and V. Meyer, that methyl anthranilate is formed when isatoic anhydride is heated with methyl alcohol in closed tubes at 150° (Abstr., 1887, 371). The yield of the ester in this reaction is equal to 28 per cent. of the anhydride used. T. A. H.

Phenylmalononitrile. JOHN C. HESSLER (*Amer. Chem. J.*, 1904, 32, 119—130).—*Ethyl phenylcyanoacetate*, $C_6H_5\cdot CH(CN)\cdot CO_2Et$, obtained by the condensation of phenylacetonitrile with ethyl carbonate, is a colourless oil which boils at 165·5° under 20 mm. and at 275° under the ordinary pressure, has a sp. gr. 1·09 at 22°, and is readily soluble in organic solvents but insoluble in water. When the ester is dissolved in aqueous solutions of alkali hydroxides, it gradually undergoes hydrolysis, forming phenylcyanoacetic acid; its solution in

aqueous ammonia slowly deposits crystals of the amide. The *sodium* derivative of the ester was obtained as a white, hygroscopic powder. *Phenylcyanoacetic acid* is a crystalline substance which melts at 92° and is soluble in water, alcohol, ether, or hot benzene; when heated at 150—160°, it undergoes decomposition with the formation of carbon dioxide and phenylacetonitrile. The *amide* separates from an alcoholic solution in large crystals, melts at 147°, and is sparingly soluble in ether or cold water.

Ethyl phenylbenzylcyanoacetate, obtained by heating ethyl phenylcyanoacetate with benzyl chloride and sodium ethoxide, is a viscid, colourless liquid which boils at 231—233° under 32 mm. and at 216—217° under 16 mm. pressure, is insoluble in water, and is not affected by aqueous alkali hydroxide; it has a sp. gr. 1·13 at 22°.

Phenylmalononitrile, prepared by the action of phosphorus pentachloride on phenylcyanoacetamide, forms large, white crystals, melts at 68—69°, boils at 152—153° under 21 mm. pressure, is readily soluble in alcohol or ether, and sparingly so in water or light petroleum; it is not readily hydrolysed even by concentrated alkali hydroxides. The *sodium* derivative was prepared and analysed. When the nitrile is treated with silver nitrate, decomposition occurs with formation of a white, amorphous *substance* melting at 147—148°.

Phenylmethylcyanoacetiminoethyl ether, obtained by the action of methyl iodide on phenylmalononitrile in presence of sodium ethoxide, is an oily substance which has a slight aromatic odour, boils at 152—153° under 16 mm. and at 158—159° under 22—23 mm. pressure, has a sp. gr. 1·06 at 23°, is readily soluble in alcohol or ether, but insoluble in water; when its alcoholic solution is treated with strong hydrochloric acid, ammonium chloride is precipitated.

Phenylbenzylmalononitrile, prepared by the action of benzyl chloride and sodium ethoxide on phenylmalononitrile, crystallises in groups of needles, melts at 97—98°, is easily soluble in ether or alcohol, and is not affected by aqueous alkali hydroxides at 100°. E. G.

[Benzylmalimides.] O. Lutz (*J. pr. Chem.*, 1904, [ii], 70, 1—18. Compare Giustiniani, Abstr., 1892, 820; Ladenburg and Herz, Abstr., 1897, i, 460).—The two optically-active and the racemic benzylmalimides are formed when the corresponding benzylmalamic acids are heated at 150° in a vacuum.

r-*Benzylmalimide* forms colourless, monoclinic crystals, melts at 118°, and, with benzoic chloride, yields *i*-benzoylbenzylmalimide, which crystallises in small, white needles, melts at 100—101°, and is identical with Giustiniani's benzoyl derivative, which melted at 100°.

d-Benzylmalimide crystallises in rhombic, prismatic needles, melts at 105°, has $[\alpha]_D + 58{\cdot}67°$ at 18°, yields *d*-benzylmalamic acid on hydrolysis, and is identical with Giustiniani's *β*-imide. The *l*-imide has similar properties.

d-*Benzoylbenzylmalimide* melts at 126—127°, and has $[\alpha]_D + 24{\cdot}7°$. The l-*compound* melts at 126—127° and has $[\alpha]_D - 24{\cdot}5°$.

l-Benzylmalimide cannot be obtained in a state of purity by heating benzylamine hydrogen malate or a mixture of benzylamine and malic acid. In each case, the product consists of a mixture of the

active and racemic substances which cannot be completely separated. Giustiniani's α-imide and Ladenburg and Herz's β-imide (m. p. 102°) were similar mixtures. G. Y.

Condensation of Imines with α-Ethylenic Ketones. CHARLES MAYER (*Bull. Soc. chim.*, 1904, [iii], 31, 985—987. Compare this vol., i, 784).—When benzylideneaniline, dissolved in alcohol, is mixed with benzylideneacetone, dissolved in the same solvent, there separates after several days triphenylpiperidone, $NPh<\begin{matrix}CHPh\cdot CH_2\\CHPh\cdot CH_2\end{matrix}>CO$, identical with that obtained by the condensation of acetone with benzylideneaniline (*loc. cit.*). This would seem to indicate that in the latter reaction the acetone first condenses with one molecule of benzylideneaniline to form the ketone, $CHPh(NHPh)\cdot CH_2Ac$, which, by the loss of one mol. of aniline, forms benzylideneacetone, which, then reacts with a second mol. of the imine, forming triphenylpiperidone. This view, however, implies that the anilinophenylbutanone first formed is unstable, which is not the case with the analogous compounds described by Francis (Trans., 1899, 75, 865; and 1902, 81, 441). T. A. H.

α-Naphthisatin-α-naphthalide and β-Naphthisatin-β-Naphthalide. CAMILLE DREYFUS and HENRY DREYFUS (D.R.-P. 152019).—Basic lead carbonate and potassium cyanide convert di-α-naphthylthiocarbamide into *α-hydrocyanocarbodinaphthylimide*,

$$C_{10}H_7\cdot NH\cdot C(CN):N\cdot C_{10}H_7,$$

which separates from benzene in yellow crystals and melts at 150°. *β-Hydrocyanocarbodinaphthylimide* is prepared in similar manner from di-β-naphthylthiocarbamide and melts at 166°. Concentrated sulphuric acid converts the imides into α-derivatives of naphthisatin, the β-compound being converted at the ordinary temperature, the α-compound preferably at 60°. When too strongly heated, insoluble products are obtained.

α-Naphthisatin-α-naphthalide, $C_{10}H_6<\begin{matrix}NH\\CO\end{matrix}>C:N\cdot C_{10}H_7$ or

$$C_{10}H_6<\begin{matrix}-N\\CO\end{matrix}>C\cdot NH\cdot C_{10}H_7,$$

forms a violet or reddish-brown precipitate. *β-Naphthisatin-β-naphthalide* dissolves in alcohol or benzene to reddish-brown solutions and melts above 180°. Heating with mineral acids removes naphthylamine, forming α- and β-naphthisatins (Hinsberg, Abstr., 1888, 372).

C. H. D.

Correction [Imino-oxymethyltriazine]. ADRIANO OSTROGOVICH (*Gazzetta*, 1904, 34, ii, 75—77).—The data previously given by the author for imino-oxymethyltriazine picrate (Abstr., 1897, i, 301) are to be corrected as follows. The picrate is formed by the action of picric acid on the base or its hydrochloride, best in presence of oxalic acid, which increases the solubility of the base in picric acid. It forms golden-yellow prisms or slender needles,

$$C_4H_6ON_4,C_6H_3O_7N_3 + H_2O,$$

melting at 121—121·5°; the anhydrous salt melts at 224—224·5°.

T. H. P.

Condensations with Amino-acids. I. THEODOR CURTIUS (*J. pr. Chem.*, 1904, [ii], 70, 57—72. Compare Abstr., 1902, i, 844).—An historical and theoretical introduction to the following papers.

G. Y.

Condensations with Amino-acids. II. Formation of Glycyl Compounds by means of Hippurazoimide. THEODOR CURTIUS and RICHARD WÜSTENFELD (*J. pr. Chem.*, 1904, [ii], 70, 73—88. Compare foregoing abstract and Abstr., 1902, i, 844).—By condensing hippurazoimide with glycine, esterifying the resulting acid, converting the ester into the hydrazide and azoimide, and repeating the foregoing operations on the latter product and another molecule of glycine, a series of acids varying from benzoylaminoacetic acid to benzoylpentaglycylaminoacetic acid has been prepared.

These acids are colourless, crystalline substances, which are only slightly soluble in alcohol or cold water, dissolve in aqueous alkalis, and yield colourless, crystalline, stable silver salts. The esters, which are best formed either by the action of ethyl iodide on the dry silver salt or by treating the acid with dilute alcoholic hydrochloric acid, are colourless, crystalline substances. The hydrazides and azoimides are colourless, crystalline substances; with increase in molecular weight, the former become less soluble in water, whilst the latter dissolve less readily in ether.

The following new substances are described.

Benzoylglycylaminoacetylbenzylidenehydrazide,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot N\colon CHPh,$$

crystallises in colourless leaflets and melts at 215—217°. *Benzoylglycylaminoacetanilide*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NHPh$, melts at 238—240°.

The *urethane*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO_2Et$, corresponding with hippenylurethane (Abstr., 1896, i, 38), is formed by the action of boiling alcohol on benzoylglycylaminoacetylazoimide. It crystallises in colourless leaflets, melts at 200°, and is hydrolysed by dilute sulphuric acid to benzoic acid, glycine, ammonia, formaldehyde, carbon dioxide, and alcohol.

Ethyl benzoyltriglycylaminoacetate,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

crystallises in colourless leaflets and melts at 213°. The *hydrazide* crystallises in small, colourless leaflets and melts at 268°; the *azoimide* melts indefinitely at 245—258°.

Benzoyltetraglycylaminoacetic acid,

$$NHBz\cdot CH_2\cdot CO\cdot [NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2H,$$

forms small, colourless leaflets and melts and decomposes at 246—252°.

Benzoylpentaglycylaminoacetic acid crystallises in leaflets and melts and decomposes at about 268°. The melting point was found to be 280—285° by Curtius and Benrath (this vol., i, 499). G. Y.

Condensations with Amino-acids. III. Formation of Glycyl Compounds by means of Hippurazoimide. THEODOR CURTIUS and LEO LEVY (*J. pr. Chem.*, 1904, [ii], 70, 89—108. Compare foregoing abstract).—Ethyl benzoyldiglycylaminoacetate is formed by the

action of hippurylazoimide on ethyl glycylaminoacetate. *Benzoyldiglycylaminoacetylbenzylidenehydrazide* crystallises in small leaflets and melts at 264—265°. Benzoyldiglycylaminoacetylazoimide is found to melt at about 236° and not at 162° as previously stated (Abstr., 1902, i, 844).

Benzoyltetraglycylaminoacetic acid is formed by the action of benzoyldiglycylaminoacetylazoimide on glycylglycine hydrochloride. When dried over sulphuric acid in a vacuum, the acid loses one mol. of water and yields a yellow, horny mass, $C_{17}H_{21}O_7N_5,H_2O$, which gives a violet coloration with Fehling's solution, melts and decomposes at 242—243°, and yields the acid when boiled with water.

Ethyl benzoyltetraglycylaminoacetate,

$$NHBz\cdot CH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2Et,$$

is formed by the action of ethyl iodide on the dry silver salt, or of benzoyldiglycylaminoacetylazoimide on ethyl glycylaminoacetate, or of benzoyltriglycylaminoacetylazoimide on ethyl aminoacetate; it melts at 244—246°. The *hydrazide* melts and decomposes at 268—269°, and its *hydrochloride*, $NHBz\cdot CH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO\cdot N_2H_3,HCl$, melts at about 252°. An azoimide of this acid has not been obtained.

Ethyl benzoylpentaglycylaminoacetate,

$$NHBz\cdot CH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_4\cdot NH\cdot CH_2\cdot CO_2Et,$$

is formed by the action of ethyl iodide on the silver salt, or of benzoyltriglycylaminoacetylazoimide on ethyl glycylaminoacetate, or of hippurylaminoacetylazoimide on ethyl triglycylaminoacetate (Curtius, this vol., i, 477). It melts at 258—263°.

Ethyl benzoylhexaglycylaminoacetate,

$$NHBz\cdot CH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_5\cdot NH\cdot CH_2\cdot CO_2Et,$$

formed from benzoyldiglycylaminoacetylazoimide and ethyl triglycylaminoacetate, is red and melts at 274—277°.

Aminoacetylhydrazide, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot NH_2$, is formed by the action of hydrazine hydrate on ethyl aminoacetate. It solidifies to a transparent, stellate mass, melts at 80—85°, and decomposes at 150°. It is moderately soluble in chloroform, less so in absolute alcohol, almost insoluble in ether or light petroleum; when exposed to air, it deliquesces and absorbs carbon dioxide. With mercuric chloride in aqueous solution, it gives a white, granular precipitate; it reduces Fehling's solution and gives a marked biuret reaction. The *hydrochloride*, $C_2H_7ON_3,2HCl$, melts at 200—201°.

The *benzylidene* derivative, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot N{:}CHPh$, crystallises in thin leaflets and melts at 157°; the *di-o-hydroxybenzylidene* derivative,

$$OH\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot CO\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OH,$$

crystallises in yellow leaflets and melts at 189—191°; the *di-β-propylidene* derivative, $CMe_2{:}N\cdot CH_2\cdot CO\cdot NH\cdot N{:}CMe_2$, crystallises in long needles, melts at about 79°, and decomposes at 215°; the *compound* with ethyl acetoacetate, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et$, commences to decompose at 280° and melts at 290°.

The *diacetyl* derivative (acetylaceturylhydrazide),

$$NHAc\cdot CH_2\cdot CO\cdot NH\cdot NHAc,$$

crystallises in microscopic needles and melts at 183·5°; the *dibenzoyl* derivative (benzoylhippurylhydrazide), $NHBz\cdot CH_2\cdot CO\cdot NH\cdot NHBz$, crystallises in small needles and melts at 213°.

Hippurylaminoacetylhydrazide,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NH_2,$$

formed by the action of hippurylazoimide on aminoacetylhydrazide, crystallises in small leaflets and melts at 230°.

The action of iodine on aminoacetylhydrazide in concentrated aqueous solution leads to the formation of a colourless *substance* which is probably the dihydrazide of glycine.

The action of sodium nitrite and hydrochloric acid on aminoacetylhydrazide in aqueous solution, under ether, leads to the formation of an ethereal solution which, with aniline, yields a substance melting at 185°. The diazotised aqueous solution after some time developed an odour of hydrazoic acid, which, on boiling, was followed by that of formaldehyde. G. Y.

Condensations with Amino-acids. IV. Action of Hippurazoimide on α-Alanine. Theodor Curtius and Emil Lambotte (*J. pr. Chem.*, 1904, [ii], 70, 109—128. Compare foregoing abstracts).—The action of hippurylazoimide on alanine in aqueous solution leads to the formation of *hippurylalanine*,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,$$

which crystallises in colourless needles and melts at 202°. It is soluble in water or alcohol, almost insoluble in ether, benzene, or chloroform; the aqueous solution reddens litmus. The *ammonium* salt crystallises in white needles; the *silver* salt crystallises in small colourless leaflets; the *copper* salt forms blue needles. The *ethyl* ester, formed by the action of ethyl iodide on the silver salt, or of dilute alcoholic hydrochloric acid on the acid, crystallises in small, colourless needles and melts at 124—126°; the *methyl* ester crystallises in small needles and melts at 136°; the *amyl* ester forms colourless leaflets and melts at 96°. The *hydrazide* crystallises in long, thin needles and melts at 187°; the *benzylidenehydrazide*,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO\cdot NH\cdot N{:}CHPh,$$

melts at 216°; the *azoimide* forms microscopic crystals, melts and decomposes at 101—102°, and, when boiled with alcohol, yields the *urethane*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot NH\cdot CO_2Et$, which crystallises from alcohol, melts at 205°, and is hydrolysed by cold dilute sulphuric acid. The *amide*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO\cdot NH_2$, melts at 195° and evolves ammonia when treated with alkalis. The action of aniline on the azoimide in alcoholic solution leads to the formation of the *phenylcarbamide* derivative,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot NH\cdot CO\cdot NHPh,$$

which forms a flocculent precipitate and melts at 216°. Its behaviour to dilute sulphuric acid is analogous to that of the urethane.

Hippuryl-α-alanyl-α-alanine,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO\cdot NH\cdot CHMe\cdot CO_2H,$$

formed by the action of hippurylalanylazoimide on alanine at −5° to −10°, forms small, colourless needles and melts at 120—130°; the *silver* salt forms leaflets which become brown on exposure to light; the *ethyl* ester melts at 174—175°; the *methyl* ester crystallises in small needles and melts at 180—181°; the *amyl* ester forms small leaflets and melts at 155°; the *hydrazide* melts at 213°; the *benzylidene-*

hydrazide melts at 238°; the *azoimide* melts and decomposes at about 145°. The action of ethyl alcohol on the azoimide leads to the formation of the *urethane*,

$NHBz·CH_2·CO·NH·CHMe·CO·NH·CHMe·NH·CO_2Et$,

which crystallises in colourless leaflets and melts at 203°; the action of ammonia on the azoimide leads to the formation of the *carbamide*, $NHBz·CH_2·CO·NH·CHMe·CO·NH·CHMe·NH·CO·NH_2$, which melts at 199°; that of aniline gives rise to the *phenylcarbamide* derivative, which melts at 226°.

Hippuryldi-α-alanyl-α-alanine,

$NHBz·CH_2·CO·NH·CHMe·CO·NH·CHMe·CO·NH·CHMe·CO_2H$,

formed from hippuryldialanylazoimide and alanine, crystallises in colourless, delicate needles and melts at 230°. G. Y.

Is α-Thiolactic Acid a Direct Decomposition Product of Proteids? KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1904, **42**, 365—370. Compare Suter, Abstr., 1895, i, 691; Friedmann, 1903, i, 75, 301).—The proteid was heated with 2—4 parts of 15 per cent. hydrochloric acid for several days at 90° in a closed flask. A 6 per cent. yield of cystin was obtained, but neither α-thiolactic acid nor its disulphide could be detected in the aqueous extracts. Minute traces of the α-thio-acid appear to be formed when the heating is prolonged and when sulphur and hydrogen sulphide begin to be formed; it is, therefore, not a primary but a secondary product of decomposition. Friedmann's acid was either formed by the action of hydrogen sulphide on pyruvic acid or by the decomposition of cystin.

The whole of the sulphur which can be eliminated by warming with sodium hydroxide is thought to be combined in the proteid molecule in the form of a cystin group. J. J. S.

Decomposition Products of Cystin. KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1904, **42**, 349—364. Compare Friedmann, Abstr., 1902, i, 731; Neuberg, *ibid.*, 743).—Both α- and β-thiolactic acids (Loven, Abstr., 1884, 1298), give the reddish-purple coloration with ferric chloride which is usually described as characteristic of thioglycollic acid. The permanent violet coloration which the α-acid gives with copper sulphate solution is best obtained by using a dilute solution of the acid and an excess of the copper sulphate, otherwise a yellowish-grey precipitate may be formed.

Suter's benzyl-α-thiolactic acid (Abstr., 1895, i, 691) melts at 76·5 and not at 74°. Benzyl-β-thiolactic acid crystallises in rhombic plates, melts at 81—81·5°, and is more readily soluble in water than the α-compound.

α-Thiolactic acid is obtained when cystin is reduced to cystein, and the hydrochloride of this is heated in aqueous solution at 140—150° and extracted with ether. β-Thiolactic acid and thioglycollic acid do not appear to be formed under these conditions, and in only one case has pyruvic acid been detected.

Among the other products obtained were hydrogen sulphide, ammonia (some 50 per cent. of the total nitrogen in cystin), and alanine.

It is probable that both β-amino-α-thiolactic acid and α-amino-β-

thiolactic acid are present in the cystin used. The former, on hydrolysis, would yield ammonia and α-thiolactic acid, the latter, hydrogen sulphide and alanine. J. J. S.

Philothion. J. DE REY PAILHADE (*Bull. Soc. chim.*, 1904, [iii], 31, 987—991. Compare Abelous and Ribaut, this vol., i, 704).—Products of the activity of living cells capable of hydrogenating sulphur at temperatures not exceeding 45° should alone be regarded as containing philothion.

The results of a number of experiments with egg-albumin coagulated under various conditions showed that the activity of the philothion is not inhibited when the albumin is coagulated alone or in presence of dilute acids, but its activity is destroyed by coagulation in presence of dilute alkalis or by the action of these substances on active coagulated albumin. The philothion of raw egg-albumin is much more susceptible to the action of acids than is that of coagulated albumin.

The discontinuous curves obtained by Abelous and Ribaut representing the influence of temperature on the rate of production of hydrogen sulphide by animal extracts (*loc. cit.*) each consists of two portions, one due to "physiological" philothion and the other to philothion condensed by coagulation.

This action of certain proteids on sulphur furnishes a method of distinguishing between serum-albumin, which is inactive, and other intracellular albumins and egg-albumin (compare Heffter and Hausmann, this vol., i, 461), and may be used for the detection of albumins of the latter class in urine, &c. Experiments in this direction with an extract from the kidney of a horse gave positive results, whereas the urines of several persons suffering from albuminuria gave negative results. T. A. H.

Thymus Nucleic Acid. I. HERMANN STEUDEL (*Zeit. physiol. Chem.*, 1904, 42, 165—170).—Neumann's α-nucleic acid (Abstr., 1900, i, 319) has been hydrolysed by boiling with hydriodic acid in the presence of phosphorous acid and the amounts of nitrogenous products determined. If the original amount of nitrogen is represented by 100, then 11·54 per cent. is found in the form of humus; 7·00 as ammonia; 3·61 as guanine; 13·45 as adenine; 6·74 as xanthine; 5·20 as hypoxanthine; 11·45 as cytosine, and 15·88 as thymine and uracil, the total nitrogen accounted for being about 75 per cent. J. J. S.

Presence in Nucleic Acids of a Radicle which yields Lævulic Acid. KATSUJI INOUYE (*Zeit. physiol. Chem.*, 1904, 42, 117—120. Compare Kossel and Neumann, Abstr., 1894, ii, 631; Noll, 1898, i, 718; and Araki, 1903, i, 668).—Lævulic acid has been obtained from the products of hydrolysis of spleen nucleic acid (compare Levene, *Zeit. physiol.*, 1902, 37, 402), of the nucleic acid from the testicles of oxen (Levene, this vol., i, 126), and of the nucleic acid from the spermatozoa of *Muraenoesox cinereus*. J. J. S.

Pure Glycogen. Z. GATIN-GRUŽEWSKA (*Pflüger's Archiv*, 1904, 102, 569—591).—Glycogen has been prepared by the Pfluger-Nerking method (Abstr., 1899, ii, 819), freed from small amounts of nitrogen derivatives by treatment with 30 per cent. potassium hydroxide on the water-bath, then diluted with water and precipitated with 97 per cent. alcohol. The precipitation with alcohol after solution in water is repeated some five or six times in order to remove all the alkali. Inorganic impurities are removed by the addition of a little acetic acid to the solution, as recommended by Bernard (*Compt. rend.*, 1857, 44, 578). After repeated precipitation with alcohol (16—18 times), the solid glycogen is washed for two days with absolute alcohol, and then with ether which is free from acid. It is desiccated over calcium chloride or phosphoric oxide, and may be dried at 100° without losing colour, but in that case should be previously heated at 60° for a day.

When dried in a vacuum desiccator over sulphuric acid, it appears to be acted on by sulphur dioxide, and is then not completely soluble in water and has a lower rotatory power. The specimens obtained were nearly all free from ash and from nitrogen. The analyses agree with the formula $C_6H_{10}O_5$, and freshly prepared specimens give $[\alpha]_D$ 196·6 (mean of four determinations). In estimating glycogen by hydrolysis with hydrochloric acid and weighing the cuprous oxide obtained with Fehling's solution, the numbers obtained should be multiplied by 0·927 (compare Nerking, Abstr., 1901, ii, 462).

The solubility of glycogen in aqueous alcohol varies considerably with the temperature, and the amount of alcohol required for precipitation diminishes with the concentration of the solution.

Clear solutions of glycogen, when placed for some time in a burette, become more concentrated in the lower part and less concentrated in the upper. Under certain conditions, the precipitated glycogen has a characteristic appearance under the microscope, and occasionally crystals of the pure compound have been obtained. Only the pure compound gives these characteristic forms, and when pure it does not adhere to glass in the same manner as a slightly impure glycogen.

J. J. S.

Guanase. WALTER JONES and C. L. PARTRIDGE (*Zeit. physiol. Chem.*, 1904, 42, 343—348).—The fact that nucleoproteids, when allowed to undergo autolysis, yield products different from those obtained by the hydrolysis of the same nucleoproteids with acids, is accounted for by the presence of an enzyme, or enzymes, which, during the autolysis, decomposes guanine into xanthine, and adenine into hypoxanthine and ultimately into xanthine. Fresh pancreas, when subjected to autolysis, does not yield adenine or guanine, and guanine which is added is transformed into xanthine within 3 days. The enzyme present in pancreas which induces this change is termed *Guanase.* A similar, or identical, enzyme exists in thymus and kidneys, but not in the spleen. Spleen contains an enzyme *adenase*, which transforms adenine into hypoxanthine in the absence of guanase. When thymus nucleoproteid is precipitated, washed with alcohol and

ether, and kept in a desiccator for 2 weeks, and then allowed to undergo autolysis, the products are adenine and guanine. J. J. S.

Colouring Matter of Blood. Formula for Hæmin. II. J. Hetper and Léon Marchlewski (*Zeit. physiol. Chem.*, 1904, **42**, 65—69. Compare this vol., i, 463; Küster, *ibid.*, 357).—Hæmin has been prepared by using propionic in place of the usual acetic acid; the product is identical with the so-called acethæmin in all physical and optical properties, and the conclusion is drawn that no acetyl groups, whether attached to O, N, or C, can be present in the hæmin ("acethæmin") molecule. The formula $C_{34}H_{33}O_4N_4ClFe$ is confirmed. J. J. S.

Melanotic Pigments. Hans Wolff (*Beitr. chem. Physiol. Path.*, 1904, **5**, 476—488).—In a melanotic liver, two pigments were separated by the use of sodium hydroxide, one being soluble, the other insoluble in this reagent. The soluble pigment has a lower percentage of carbon than most melanins, and contains iron; the other contains no iron and only traces of sulphur. From another strongly melanotic liver, a pigment was separated the individuality of which was attested by analyses. It contains at least 15 per cent. of a hydro-aromatic substance which is shown to be identical with xylitone; *iso*valeronitrile was also prepared from it in amount corresponding with 2·5 per cent. of the melanin; a third product which was isolated could not be identified. No sulphur-yielding substance was obtained by oxidation, so nothing can be said of the way the sulphur is combined. The pigment contains 1·7 per cent. of sulphur.

W. D. H.

Action of Heat and Acidity on Dissolved Amylase. Paul Petit (*Compt. rend.*, 1904, **138**, 1716—1718. Compare this vol., i, 541).—An aqueous infusion of malt, on being heated at 100°, coagulates, thickens without coagulation, or remains limpid, according to the amount of free acid present in the original solution. Representing the acidity which promotes coagulation by unity, the other two values are represented by 2 and 3 respectively when hydrochloric acid is the acid added, or 3 and 6 respectively when lactic acid is added. The action of heat on the infusions is to cause an increase in the acidity up to the point where coagulation begins. The diastatic power of malt infusions varies with the acidity, reaching a maximum for that quantity of acid which determines the beginning of coagulation. M. A. W.

Action of Maltase. Stability of the Ferment. Influence of the Products of the Reaction. Mlle. Ch. Philoche (*Compt. rend.*, 1904, **138**, 1634—1636. Compare this vol., ii, 318).—The velocity of hydrolysis by maltase (taka-diastase) of solutions containing varying proportions of maltose and dextrose was measured polarimetrically and it was found that the ferment retains its initial activity during a period of 38 hours in the presence of the products of the reaction. The presence of dextrose retards the hydrolysis, thus the rotatory power, after 30 hours, of a solution initially containing 4 per cent. of

maltose was 4·12°, and the addition of 10 or 20 per cent. of dextrose to a similar solution lowered the rotatory power to 2·92° and 2·77° respectively. M. A. W.

Existence in Plants of an Oxidising-reducing Diastase. Conditions of its Action. J. E. Abelous (*Compt. rend.*, 1904, **138**, 1619—1620. Compare Abstr., 1903, ii, 560; this vol., ii, 188, 283).—The oxidising-reducing diastase present in the potato converts salicylaldehyde into salicylic acid under conditions in which the normal diastases are inoperative, namely, in the absence of air, and when the vegetable cells are not destroyed by pressure.

M. A. W.

Formation of Carbamide by Fermentations. Albrecht Kossel and Henry D. Dakin (*Zeit. physiol. Chem.*, 1904, **42**, 181—188. Compare this vol., ii, 425).—The reactions of arginase with precipitating agents and solvents are not exactly the same as those of lieno-α- or -β-protase (Hedin, *Jour. Physiol.*, **30**, 155). Liver has the greatest power of decomposing arginine; nerves, thymus, and lymph glands are also active, but blood and muscles have practically no action.

The proton (*loc. cit.*) obtained from clupein is termed β-clupeon. It differs from Kossel and Goto's α-clupeon in yielding only 69·7 per cent. of its total nitrogen as arginine instead of 80. On hydrolysis with dilute sulphuric acid, β-clupeon yields ornithine, whereas clupein does not. J. J. S.

Animal Lactase. H. Bierry and Gmo-Salazar (*Compt. rend.*, 1904, **139**, 381—384).—The juices from the pancreas and the intestine do not contain any of the lactose-splitting enzyme. The fluid obtained by maceration of intestinal mucus only shows the presence of lactase if cellular elements are present, or if the fluid has been in contact with these *in vitro* for a sufficiently long time. In the case of the dog, lactase has been found in the small intestine, but not in the stomach or the large intestine; it is also present in the fœtus of the cow or ewe. The activity of animal lactase is favoured by slight acidity (0·02—0·04 gram of hydrochloric or acetic acid per litre). A larger quantity (0·5—1 gram per litre) stops the action completely. Alkalis have a retarding effect when present to the extent of a few centigrams per litre. H. M. D.

Organic Chemistry.

Addition of Bromine to Carbon Atoms united by a Double Linking. Hugo Bauer (*Ber.*, 1904, 37, 3317—3321).—Observations made by other investigators on the addition of bromine in diffused daylight are brought together and the following generalisations drawn. In the system $CO_2H\cdot CH\colon CH_2$, bromine is added so long as all three hydrogen atoms are not replaced by bromine or by bromine and methyl. With three methyl groups, for example, trimethylacrylic acid, the power of uniting with bromine is still retained (W. H. Perkin, jun., Trans., 1896, 69, 1480).

With two carboxyl groups, for example, $CO_2H\cdot CH\colon CH\cdot CO_2H$, addition is possible so long as both hydrogen atoms are not replaced by bromine or methyl, for example, dimethylfumaric, dibromofumaric, and bromomesaconic acids do not form dibromides. Ethylenetetracarboxylic acid and tetraphenylethylene do not unite with bromine.

In styrene, $C_6H_5\cdot CH\colon CH_2$, addition of bromine is possible when all three hydrogens are replaced by methyl. With stilbene, $C_6H_5\cdot CH\colon CH\cdot C_6H_5$, addition is no longer possible when the two hydrogens are replaced by bromine. With $CPh_2\colon CH_2$, the replacement of one hydrogen by bromine is sufficient to prevent the addition of bromine, but if one or both hydrogens are replaced by methyl, addition can still take place. J. J. S.

αε-Dibromopentane. Julius von Braun (*Ber.*, 1904, 37, 3210—3213).—αε-Dibromopentane is conveniently prepared in quantity by heating benzoylpiperidine with phosphorus pentabromide and fractionating the resulting mixture under reduced pressure; it boils at 220—222° or at 104—105° under 14 mm. pressure and reacts with aniline to form 1-phenylpiperidine (compare Lellmann, Abstr., 1887, 604) boiling at 257—258°. E. F. A.

Decomposition of Di-iodoacetylene. Rudolf Schenck and J. Litzendorff (*Ber.*, 1904, 37, 3453—3464. Compare Baeyer, Abstr., 1885, 1199; Meyer and Pemsel, *ibid.*, 1896, i, 517).—The di-iodoacetylene used was prepared by Biltz's method (Abstr., 1897, i, 389), and also from tetraiodoethylene by Nef's method (*Annalen*, 1897, 298, 341). When the di-iodoacetylene is heated in benzene solution at 100°, carbon is deposited; this, however, is not pure but contains iodine compounds and benzene, which are only removed by heating the carbon in a current of hydrogen at a relatively high temperature.

The equilibrium $C_2I_4 \rightleftarrows C_2I_2 + I_2$ has been determined by heating a solution of tetraiodoethylene in benzene at 138° for different lengths of time. Equilibrium is attained after about 4 hours when 4 per cent. of the tetraiodo-compound is decomposed. When ethylene dibromide is used as solvent, equilibrium is reached when 8·8 per cent. is decom-

posed. Previous heating of the solution at 55° has no effect, whereas equilibrium is attained in a much shorter time in tubes previously exposed to sunlight.

The decomposition of di-iodoacetylene, $2C_2I_2 = C_2I_4 + C_2$, has been investigated in various solutions and at different temperatures by weighing the amount of carbon deposited. In all cases, before weighing, the carbon was heated in a stream of hydrogen. The results indicate that the reaction is unimolecular, and constants have been obtained by aid of the equation $K = 1/t \log a/a - x$. The influence of temperature is shown by the following numbers obtained for benzene solutions: 100°, $K = 0·0002$; 110°, $K = 0·00047$; 138°, $K = 0·0071$. The influence of the solvent is not so marked, the smallest numbers were obtained with toluene solutions.

The reaction is considerably accelerated by the presence of catalysers, more especially of solid mercuric iodide. In the presence of this reagent, the constant tends to increase with the time, probably owing to the fact that more of the catalyser dissolves in the solvent (benzene) as the time proceeds.

The nature of the glass does not appear to affect the rate of decomposition.

When benzene solutions of di-iodoacetylene are heated at 100°, it is found that the solutions can remain quite clear for several hours and then the deposition of carbon begins suddenly, and during the next half hour a considerable amount of decomposition occurs. It is probable that the finely divided carbon itself acts as a catalyser and that the decomposition takes place on the surface of this precipitated carbon.

Good photographic paper can be made by impregnating paper with a benzene solution of di-iodoacetylene. The great drawback is the obnoxious odour.

The decomposition of di-iodoacetylene by alcoholic potash (compare Nef, *loc. cit.*) is regarded as a reaction between nascent carbon and alkali and is thus comparable with the action of other non-metals, for example, chlorine, sulphur, and phosphorus, on alkalis. J. J. S.

α-Derivatives of Geraniol. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P. 153120).—α-Alkyl- or -aryl-geraniols may be prepared from citral and magnesium alkyl or aryl haloids, the resulting double compounds being decomposed by water or dilute acids. When strong acids are employed, hydrocarbons are produced (Grignard, Abstr., 1901, i, 679). *α-Ethylgeraniol*,

$$CMe_2:CH·CH_2·CH_2·CMe:CH·CHEt·OH,$$

boils at 120° under 14 mm. pressure. *α-Methylgeraniol* is a colourless liquid boiling at 112—113° under 12 mm. pressure. *α-Phenylgeraniol* is a slightly yellow, highly refracting oil, boiling at 175—176° under 12 mm. pressure. The rose-like odour of these oils is stronger than that of geraniol. C. H. D.

A Crystalline Compound of Lead Thiosulphate and Acetate, $2PbS_2O_3,Pb(C_2H_3O_2)_2$. PAUL LEMOULT (*Compt rend.*, 1904, 139, 422—424).—Lead thiosulphate, obtained by adding a solution of lead

acetate to one of sodium thiosulphate, dissolves in acetic acid, and from the solution a double salt having the composition $2PbS_2O_3,Pb(C_2H_3O_2)_2$ separates in the form of hard, thin, white, needle-shaped crystals 3 to 4 mm. long, very slightly soluble in cold water, less so in dilute acetic acid, and more so in boiling water, from which it can be crystallised.

M. A. W.

Theory of Saponification. RICHARD FANTO (*Monatsh.*, 1904, 25, 919—928. Compare Geitel, Abstr., 1897, ii, 547; Balbiano, this vol., i, 216).—The author has been unable to find a solvent which, whilst not entering into the reaction, will permit the hydrolysis of triglycerides to be carried out in a homogeneous solution. In several experiments on the partial hydrolysis of triglycerides, the glycerol obtained corresponded with the potassium hydroxide which was neutralised; neither di- nor mono-glycerides could be detected amongst the products, and if these are formed in the course of the reaction they must immediately undergo further hydrolysis. The saponification of triglycerides by potassium hydroxide is, at least seemingly, a quadrimolecular reaction.

G. Y.

Synthesis of Stearic Acid by means of the Electric Discharge. ALEXANDRE DE HEMPTINNE (*Bull. Acad. Roy. Belg.*, 1904, 550—556).—Under the influence of the electric discharge, oleic acid is converted into stearic acid to the extent of about 50 per cent. in 10 hours. The apparatus used is described in detail. E. F. A.

Formation of Complex Salts with Thio-acids. Thioglycollates. ARTHUR ROSENHEIM and ISSER DAVIDSOHN (*Zeit. anorg. Chem.*, 1904, 41, 231—248).—The majority of investigations with complex salts have hitherto been conducted with salts where the cathion is complex. The authors have examined cases where the anion is complex and contains sulphur, with the view of determining whether thio-acids form complex compounds with such electronegative elements, which otherwise exhibit little tendency to the formation of complexes. The metallic derivatives of ethyl xanthate studied by Hasliwetz do not suffer normal dissociation.

When an alcoholic solution of potassium xanthate is boiled with an excess of cobaltous chloride, dark green needles separate, which Hasliwetz supposes to be cobaltous xanthate; the compound is, however, a cobaltic salt, $(OEt{\cdot}CS_2)_3Co$. The nickel salt, prepared in an analogous manner, has the composition $(OEt{\cdot}CS_2)_2Ni$.

Solutions of thioglycollic acid or of its sodium and potassium salts are very readily oxidised. The analysis of the thioglycollates described was accordingly conducted iodometrically, the reaction of the salts dissolved in a solution of sodium hydrogen carbonate and acted on by iodine being expressed as follows:

$$2SH{\cdot}CH_2{\cdot}CO_2Na + I_2 = CO_2Na{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CO_2Na + 2HI.$$

Monosodium thioglycollate, $SH{\cdot}CH_2{\cdot}CO_2Na,3H_2O$, prepared from sodium hydrosulphide and monochloroacetic acid, separates in needles

and has a neutral reaction. When dried over sulphuric acid, it forms its *monohydrate*, $SH\cdot CH_2\cdot CO_2Na,H_2O$. *Disodium thioglycollate*,

$$SNa\cdot CH_2\cdot CO_2Na,2H_2O,$$

separates in prisms and has an alkaline reaction. *Magnesium thioglycollate*, $CH_2<\begin{matrix}CO_2\\S\end{matrix}>Mg,8H_2O$, crystallises in prisms. *Manganese thioglycollate* contains $7H_2O$ and separates in pink prisms. *Zincothioglycollic acid*, $Zn(S\cdot CH_2\cdot CO_2H)_2,H_2O$, prepared by the action of zinc on thioglycollic acid, separates in needles. *Sodium zinc thioglycollate*, $Na_2Zn_2(C_2H_2O_2S)_3,4H_2O$, forms needles. *Barium zinc thioglycollate*, $BaZn_2(C_2H_2O_2S)_3,3H_2O$, is formed from the preceding salt by the addition of barium chloride. The two latter salts are derivatives of a complex zinc thioglycollic acid, the zinc being in the complex anion. For comparison, zinc alkali thiosulphates were prepared. *Potassium zinc thiosulphate*, $K_2Zn(S_2O_3)_2,H_2O$, and *ammonium zinc thiosulphate*, $(NH_4)_2Zn(S_2O_3)_2,H_2O$, separate from water in prisms; both salts are very soluble in water and give the reactions for the zinc ion, which the corresponding glycollates do not.

The *double* salt of cadmium thioglycollate and sodium chloride, $Cd(S\cdot CH_2\cdot CO_2Na)_2,3NaCl,6H_2O$, separates in prisms and may be crystallised from water without change. *Barium cadmiothioglycollate*, $Cd(S\cdot CH_2\cdot CO_2)_2Ba,18H_2O$, is crystalline. *Sodium nickelothioglycollate*, $Ni(S\cdot CH_2\cdot CO_2Na)_2,4H_2O$, forms green needles. In contradistinction to the zinc and cadmium salts described, the nickel in the complex is only feebly bound, since solutions of the salt readily give the reactions for the nickel ion. The *cobalt thioglycollate* prepared,

$$[Co(S\cdot CH_2\cdot CO_2)_2]_2CoH_2,11H_2O,$$

is the hydrogen cobaltous salt of cobaltothioglycollic acid,

$$Co(S\cdot CH_2\cdot CO_2H)_2.$$

Sodium cobaltothioglycollate, $Co(S\cdot CH_2\cdot CO_2Na)_2,6H_2O$, forms dark reddish-brown needles with a green lustre. *Barium cobaltothioglycollate*, $Co(S\cdot CH_2\cdot CO_2)_2Ba,12H_2O$, is dark brown. The three latter salts do not exhibit the reactions of the cobalt ion.

Ammonium cobaltothiosulphate, $(NH_4)_6Co_2(S_2O_3)_5,6H_2O$, forms greenish-blue prisms, solutions of which give the reactions for the cobalt ion.

Sodium lead thioglycollate, $[Pb(S\cdot CH_2\cdot CO_2)_2]_2PbNa_2,2H_2O$, forms yellow needles; addition of sodium hydroxide to its solution causes no precipitate. *Sodium copper thioglycollate*, $Na_3Cu_5(C_2H_2O_2S)_4.H_2O$, separates in greenish-white needles. *Sodium silver thioglycollate*, $Na_4Ag_2(C_2H_2O_2S)_3$, has an alkaline reaction; when potassium hydroxide is added to its solution, no precipitate is formed. When silver chloride is dissolved in ammonium thioglycollate, iridescent needles of *ammonium silver glycollate*, $SAg\cdot CH_2\cdot CO_2NH_4$, separate. When dissolved in ammonium thioglycollate, the *salt*,

$$Ag(S\cdot CH_2\cdot CO_2)_2(NH_4)_2H,9H_2O,$$

separates in needles.

Bismuth thioglycollate, $Bi(S\cdot CH_2\cdot CO_2H)_3$, separates in dark yellow crystals. *Bismuth bismuthothioglycollate*, $Bi(S\cdot CH_2\cdot CO_2)_3Bi$, is a dark yellow, crystalline powder. The *salt*,

$$Bi(S\cdot CH_2\cdot CO_2H)_3,3(SH\cdot CH_2\cdot CO_2H),5H_2O,$$

crystallises in yellow needles. The addition of water to these bismuth salts causes no precipitate of basic salts and the addition of ammonia no precipitate of hydroxide, but their alkaline solutions undergo gradual decomposition.

Potassium bismuthothioglycollate, $Bi(S \cdot CH_2 \cdot CO_2K)_3,6H_2O$, crystallises in yellow prisms. The *salt*, $OH \cdot Bi(S \cdot CH_2 \cdot CO_2Na)_2,10H_2O$, forms yellow needles.

Antimoniothioglycollic acid, $Sb(S \cdot CH_2 \cdot CO_2H)_3,12H_2O$, crystallises in transparent pyramids.

Arseniothioglycollic acid, $As(S \cdot CH_2 \cdot CO_2H)_3,\frac{1}{2}H_2O$, forms transparent tetrahedra.

The "Komplexzerfallkonstante" of several of the thioglycollates described were determined by von Euler (compare Abstr., 1903, ii, 544, 717; this vol., ii, 11, 379). Those values for sodium cadmium thioglycollate and sodium lead thioglycollate respectively are at least 10^6 times as small as the values for the corresponding thiosulphates.

A. McK.

Antimony Double Lactates. B. Moritz (*Zeit. angew. Chem.*, 1904, **17**, 1143—1148).—Polemical. A reply to Jordis (Abstr., 1902, i, 740; this vol., i, 468). A. McK.

Condensations by means of Magnesium Ethyl Iodide. Adolf Franke and Moritz Kohn (*Monatsh.*, 1904, **25**, 865—870. Compare Kling, this vol., i, 2).—The action of magnesium ethyl iodide on the aldol from formaldehyde and *iso*butaldehyde (Wessely, Abstr., 1900, i, 428) leads to the formation of an *ester* of Just's pentaglycol (Abstr., 1896, i, 413) and hydroxypivalic acid,

$$OH \cdot CH_2 \cdot CMe_2 \cdot CH_2 \cdot O \cdot CO \cdot CMe_2 \cdot CH_2 \cdot OH,$$

which separates from light petroleum in stellate aggregates of crystals, melts at 51°, and boils at 156° under 10 mm. pressure. When hydrolysed with aqueous potassium hydroxide, the ester yields pentaglycol and hydroxypivalic acid.

Along with the ester there are formed trioxymethylene, the last traces of which can be separated from the ester only by prolonged boiling in a reflux apparatus, and a viscid, colourless oil, which boils at 110° under 10 mm. and at 200—220° under atmospheric pressure.

G. Y.

Acetylation of Ethyl Cyanoacetate. Walter Dieckmann and Fritz Breest (*Ber.*, 1904, **37**, 3384—3387).—Ethyl cyanoacetate yields ethyl cyanoacetoacetate when boiled with acetic anhydride and sodium acetate, and when treated with acetic anhydride and pyridine or with acetyl chloride and pyridine in the cold (compare Claisen and Haase, Abstr., 1900, i, 373). The best yield, 60 per cent. of the theoretical, is obtained by the interaction of ethyl cyanoacetate (1 mol.), pyridine (2 mols.), and acetic chloride ($1\frac{1}{2}$ mols.). The product is isolated as the green *copper* compound, $(C_7H_8O_3N)_2Cu$, which crystallises from a mixture of alcohol and chloroform and melts at 235°. On prolonged boiling with acetic anhydride and pyridine, ethyl cyanoacetate yields cyanoacetylacetone.

Ethyl cyanoacetate does not form ethyl cyanoacetoacetate when boiled with acetic anhydride and quinoline or dimethylaniline.

G. Y.

Constitution of Ethyl Acetoacetate. LUDWIG KNORR (*Ber.*, 1904, **37**, 3488—3489. Compare Abstr., 1899, i, 673).—In the light of the results obtained by Knorr and Hörlein (see succeeding abstract), the non-occurrence of the ammonia reaction with ethyl acetoacetate is no proof of the absence of the enolic modification, and the author's former conclusion, that the enolic and ketonic modifications exist together in a state of equilibrium, is probably correct.

C. H. D.

The Application of Hantzsch's Ammonia Reaction to the Enolic Forms of Ethyl Diacetylsuccinate. LUDWIG KNORR and H. HÖRLEIN (*Ber.*, 1904, **37**, 3490—3493).—The seven known modifications of ethyl diacetylsuccinate, five of which are enolic, yield no precipitate with ammonia in ethereal solution. A solution of the β-ester in ether, which had been heated at 120°, gave an amorphous precipitate of ammonium ethyl *iso*carbopyrotritarate with ammonia. Ethyl *iso*carbopyrotritarate is known to be formed on heating ethyl diacetylsuccinate. The statement of Hantzsch and Dollfus (Abstr., 1902, i, 233, 675) that the enolic modifications of ethyl diacetylsuccinate yield precipitates with ammonia in ethereal solution is erroneous, and is due to the presence of acid impurities in the ester employed by them. Hantzsch's ammonia reaction is, therefore, not a trustworthy method of distinguishing ketonic from enolic compounds, but may be used to distinguish strongly enolic compounds, such as the hydroxymethylene derivatives, from weak enols.

C. H. D.

Constitution of Dehydracetic Acid. WALTER DIECKMANN and FRITZ BREEST (*Ber.*, 1904, **37**, 3387—3392).—When boiled with acetic anhydride in presence of a trace of acetic chloride, triacetic-δ-lactone forms an *anhydride*, $O<{CO-CH \atop CMe:CH}>C\cdot O\cdot C<{CH-CO \atop CH:CMe}>O$, which is a viscid oil. It boils at 172—174° under 16 mm. pressure, gives no reaction with ferric chloride, and is easily hydrolysed by aqueous sodium carbonate; when boiled with acetic anhydride and sodium acetate or pyridine (compare Collie, Trans., 1900, **77**, 971), triacetic-δ-lactone forms dehydracetic acid. The action of formaldehyde on triacetic-δ-lactone, in aqueous or alcoholic solution, leads to the formation of *methylenebis-triacetic-δ-lactone*, $\begin{array}{l} O-CO-CH\cdot CH_2\cdot CH\cdot CO\cdot O \\ CMe:CH\cdot CO \quad\quad CO\cdot CH:CMe \end{array}$, which crystallises in colourless, slender needles, melts and decomposes at 245°, gives a brownish-red coloration with ferric chloride in alcoholic solution, and, on titration, with phenolphthalein as indicator, neutralises about $1\frac{1}{2}$ mols. of alkali hydroxide (compare Wolff, Abstr., 1901, i, 283).

C-Carbanilinotriacetic-δ-lactone, $\begin{array}{l} O-CO-CH\cdot CO\cdot NHPh \\ CMe:CH\cdot CO \end{array}$, formed when molecular proportions of triacetic-δ-lactone and phenylcarbimide

are warmed with sodium acetate, crystallises in thick, colourless prisms, melts at 156°, is easily soluble in aqueous alkali hydroxides, gives an intense yellowish-red coloration with ferric chloride, and forms slightly soluble crystalline *sodium* and *copper* salts. With phenylcarbimide alone, triacetic-δ-lactone forms an O-*derivative.* Dehydracetic acid does not enter into reaction with phenylcarbimide in presence of sodium acetate.

The resemblance of triacetic-δ-lactone to the dihydroresorcinols, and of dehydracetic acid to the *C*-acetyl derivatives of the dihydroresorcinols, supports Feist's formula for dehydracetic acid (Abstr., 1892, 584), $\begin{array}{l} \mathrm{O{-}CO{-}CH{\cdot}Ac} \\ \mid \qquad\quad\;\, \mid \\ \mathrm{CMe{:}CH{\cdot}CO} \end{array}$. G. Y.

Claisen's Transformation of *O*-Acyl Derivatives of Ethyl Acetoacetate into the Isomeric *C*-Acyl Derivatives. WALTER DIECKMANN and RICHARD STEIN (*Ber.*, 1904, 37, 3392—3396. Compare Claisen and Haase, Abstr., 1901, i, 118).—When warmed for 7 hours with 0·1 gram of sodium and 1 gram of ethyl acetoacetate in absolute ethereal solution, 8 grams of ethyl *O*-acetylacetoacetate yield 1 gram of ethyl diacetoacetate, the action taking place in proportion to the sodium present. When warmed for 15 minutes with 1·1 grams of sodium and 6·5 grams of ethyl acetoacetate, 8·5 grams of ethyl *O*-acetylacetoacetate yield 3 grams of ethyl diacetoacetate. Nine grams of ethyl *O*-acetylacetoacetate, boiled for 16 hours with 0·4 gram of sodium in ethereal solution, yields 1·9 grams of ethyl diacetoacetate and 0·8 gram of ethyl acetoacetate. Eight grams of ethyl *O*-acetylacetoacetate, warmed for $4\frac{1}{2}$ hours with ethyl sodiobenzoylacetate prepared from 1·1 grams of sodium and 9 grams of ethyl benzoylacetate in ethereal solution, yields 2 grams of ethyl diacetoacetate and 3 grams of ethyl *C*-acetylbenzoylacetate. A similar result was obtained by using $1\frac{1}{2}$ mols. of potassium carbonate instead of 1 atom of sodium. These results show that, contrary to Erlenmeyer's view (Abstr., 1901, i, 357), the reaction takes place between a molecule of the *O*-acyl compound and a molecule of the sodio-compound.

Ethyl sodioacetoacetate has no action on ethyl *O*-acetylacetoacetate in ethereal solution, cooled by ice. If an ethereal suspension of ethyl sodioacetoacetate, prepared from 16 grams of ethyl acetoacetate, is poured into twice its volume of ice-cooled acetyl chloride, diluted with ether, it yields, after 20 minutes, 8 grams of ethyl diacetoacetate. This points to the primary formation of the *C*-acetyl derivative by the action of acetyl chloride on the sodio-compound (compare Claisen, Abstr., 1894, i, 31). G. Y.

Action of Nitrous Acid and its Derivatives on α-Substituted β-Ketonic Esters. Part I. General. Part II. Preparation of α-Oximino-esters and Acids. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1049—1055 and 1055—1061. Compare Abstr., 1902, i, 704, 705).—The observations of Meyer and Zublin (Abstr., 1878, 487 and 659), Treadwell and Westenberger (Abstr., 1883, 572), and Ceresole (Abstr., 1882, 1052) on the action of nitrous acid on these esters are reviewed. For the preparation of

the oximino-esters resulting from this reaction, the following methods are recommended. The α-substituted ester is dissolved in twice its weight of sulphuric acid, care being taken to keep the temperature below 0°; the mixture is kept for two hours at 0° and then nitrosyl-sulphuric acid, dissolved in twice its weight of sulphuric acid, is added very gradually. This mixture is poured on ice and the resulting oximino-compounds extracted with ether. The ethereal solution is washed, first with a solution of sodium carbonate, to remove the oximino-acid simultaneously formed, then with water, and finally the solvent is distilled off and the residue purified by fractional distillation. The yield of ester varies from 85 to 90 per cent., but may be largely replaced by the oximino-acid if the temperature is allowed to rise above 0°, when the β-ketonic ester is dissolved in sulphuric acid. Where it is inconvenient to use sulphuric acid as a solvent, formic or acetic acid may be substituted. When nitrosyl chloride is used in place of "chamber crystals" the reaction is complex and varies with the conditions of the experiment. Nitrous esters in conjunction with sodium alkyloxides may also be employed, but the alkyl group in the nitrite must be the same as that in the ketonic ester used, otherwise substitution may occur. This method is generally applicable, but the yields obtained are less satisfactory and the operation more troublesome than that first described. T. A. H.

Theory of the Transformation of α-Substituted β-Ketonic Esters into α-Oximino-esters. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1061—1067. Compare preceding abstract).—When nitrosyl chloride is passed into well-cooled methyl methylacetoacetate, $CHAcMe\cdot CO_2Me$, the odour of acetyl chloride becomes noticeable; if the mixture is then warmed, hydrogen chloride is evolved, and from the residue an oil (b. p. 125° under 14 mm. pressure), which is probably a mixture of methyl α-oximinopropionate with its acetyl derivative, is obtained. Similarly, when dry ammonia is passed into the product obtained by the action of nitrosyl chloride on methyl benzoyl-α-methylacetate, methyl oximinopropionate and benzamide (b. p. 182—183° under 1 mm. pressure) are formed.

When α-substituted β-ketonic esters are treated with nitrosyl-sulphuric acid, the reaction proceeds according to the equation:

$$R\cdot CO\cdot CHR'\cdot CO_2Et + SO_2(NO_2)\cdot OH = R\cdot CO_2H + CR'(CO_2Et):N\cdot O\cdot SO_2OH;$$

thus methyl benzoylmethylacetate, $CHBzMe\cdot CO_2Me$, gives under these conditions benzoic acid and methyl α-oximinopropionate. When the same ester is treated with methyl nitrite in presence of sodium methoxide, the benzoic acid is eliminated as methyl benzoate.

It is remarkable that in all the foregoing reactions α-substituted β-ketonic esters are converted into α-oximino-esters, whereas according to Ceresole (Abstr., 1882, 1052) the action of nitrous acid on these esters gives rise to the monoxime of the α-diketone. This difference is probably due to the fact that in the reactions now described the β-ketonic esters are converted by the solvents employed into derivatives of the enolic forms of the esters, and it is suggested that the

solutions in sulphuric acid contain acid sulphates of these enolic forms, for example, $HO\cdot SO_2\cdot O\cdot CR\colon CR'\cdot CO_2H$. Adopting this explanation, the following rule may be given. *When the enolic form of an α-substituted β-ketonic ester is treated with nitrous acid or its derivatives it is converted into an α-oximino-ester.* T. A. H.

α-Oximino-derivatives of Homologues of Pyruvic Acid and its Esters. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1068—1075. Compare Bouveault and Locquin, Abstr., 1902, i, 704, 705).—The following compounds were prepared by the action of nitrosyl-sulphuric acid on the appropriate α-alkylacetoacetic ester as described in the preceding abstracts.

Methyl α-oximinopropionate, $NOH\colon CMe\cdot CO_2Me$, furnishes an *acetyl* derivative which melts at 42° and boils at 126° under 14 mm. pressure. The *butyryl* derivative, obtained as a liquid by the action of butyryl chloride on the oxime, distils at 153—155° under 16 mm. pressure, but could not be obtained pure. The *benzoyl* derivative melts at 103° (corr.), boils and decomposes at about 190° under 12 mm. pressure, and is resolved into its generators by solution in sulphuric acid at 0°. α-Oximinobutyric acid, $NOH\colon CEt\cdot CO_2H$, obtained by hydrolysing the ethyl ester (Lepercq, *loc. cit.*, and Bouveault and Locquin, Abstr., 1902, i, 704), crystallises in colourless needles and melts at 169—170° (corr.) (compare Hantzsch and Wild, Abstr., 1896, i, 285).

Ethyl α-oximino*iso*valerate, $NOH\colon CPr^{\beta}\cdot CO_2Et$, melts at 57° and boils at 129° under 13 mm. pressure (compare Bouveault and Wahl, Abstr., 1902, i, 137); the corresponding acid volatilises and decomposes at 150°, but melts on the mercury-bath at 171—172° (corr.).

Ethyl α-oximinovalerate, $NOH\colon CPr^{\alpha}\cdot CO_2Et$, melts at 48° and boils at 144—145° under 16 mm. pressure. iso*Butyl α-oximinovalerate*, $NOH\colon CPr^{\alpha}\cdot CO_2\cdot C_4H_9$, prepared from *iso*butyl propylacetoacetate (sp. gr. 0·954 at 0°/4° and b. p. 115—116° under 13 mm. pressure), boils at 152° under 15 mm. pressure and melts at 16°. With this compound there is formed some *iso*butyl α-ketovalerate. α-Oximinovaleric acid forms small, white crystals, melts and decomposes at 155° (corr.), and sublimes at 145° (compare Fürth, Abstr., 1884, 42). The metallic salts are soluble in water. *Ethyl α-oximino*iso*hexoate* melts at 60° and boils at 142° under 12 mm. pressure. The corresponding acid (Miller and Plochl, Abstr., 1893, i, 502) melts at 153—154° (corr.); it furnishes a crystalline *silver* salt. *Ethyl α-oximino*iso*heptoate*, prepared from ethyl *iso*amylacetoacetate (Abstr., 1904, i, 646), boils at 156° under 16 mm. pressure and has sp. gr. 0·911 at 0°/4°. The corresponding *acid* melts at 163—164° (corr.); the *sodium* salt is crystalline. *α-Oximinodecoic acid* (methylhexylpyruvic acid oxime) crystallises from a mixture of ether and light petroleum, melts at 89—90° (corr.), and is soluble in organic liquids (Abstr., 1902, i, 704). T. A. H.

Electrolytic Reduction of Carboxylic Acids and their Esters in Sulphuric Acid Solution. JULIUS TAFEL and GUSTAV FRIEDRICHS (*Ber.*, 1904, 37, 3187—3191).—Oxalic acid is reduced

electrolytically in presence of sulphuric acid to glyoxylic acid, the change being nearly quantitative. Other dicarboxylic acids, such as malonic, succinic, and tartaric acids, as well as most monocarboxylic acids, remain unaltered. On the other hand, the esters of oxalic, malonic, acetoacetic, benzoic and phthalic acids are all easily reduced electrolytically: thus ethyl benzoate is reduced to benzyl ethyl ether, boiling at 187—189°, and methyl benzoate to benzyl methyl ether boiling at 169°, both under 732 mm. pressure. In the case of ethyl oxalacetate and ethyl benzoylacetate, apparently only the keto-group is attacked, as only 2 atoms of hydrogen are used. Ethyl oxalate requires 4 atoms of hydrogen in aqueous and only 2 in alcoholic solution.

E. F. A.

Aqueous Solutions of Magnesium Oxalate. FRIEDRICH KOHLRAUSCH and FRANZ MYLIUS (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1223—1227).—Solutions of magnesium oxalate were prepared by saturating an oxalic acid solution with magnesium hydroxide, filtering, and neutralising by means of a drop of oxalic acid. By this means a 10 per cent. solution could be prepared, that is, a solution of about 300 times the concentration of the saturated solution of $MgC_2O_4,2H_2O$. The solution, however, soon becomes turbid. A solution of concentration 1·1753 per cent., although 30 times as concentrated as the saturated solution, is sufficiently stable to allow its conductivity to be determined, as after a fortnight it is still 1·5 times super-saturated. The conductivities from $0·209N$ to $0·0000266N$ solutions were determined by diluting such a solution. The limiting value calculated from the migration velocities agrees well with that deduced from the determinations. The equivalent conductivity sinks very rapidly with increase of concentration, whilst the temperature-coefficient is also very low. The author considers that these results indicate the formation of molecular complexes in the solutions.

L. M. J.

Electrolysis of Dicarboxylic Organic Acids: Glutaric Acid. L. VANZETTI (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 112—120).—On electrolysing a 20 per cent. solution of potassium glutarate in an atmosphere of carbon dioxide, the voltage being 10 and the current 2—2½ amperes, the gas formed was found to be propylene; no trimethylene was obtained, although this might have been expected.

T. H. P.

Complex Compounds of Molybdic Acid and of Tungstic Acid with Organic Acids. HERMANN GROSSMANN and HANS KRÄMER (*Zeit. anorg. Chem.*, 1904, **41**, 43—60. Compare Abstr., 1903, i, 549).—From the determinations of electrical conductivity quoted, it appears that in solutions which contain sodium molybdate, Na_2MoO_4 (1 mol.), or sodium tungstate, Na_2WO_4 (1 mol.), mixed with oxalic acid (1 mol.), tartaric acid (1 mol.), or malic acid (1 mol.), normal salts of dibasic acids are produced, which in dilute solution suffer considerable hydrolytic dissociation; this hydrolytic dissocia-

tion is more marked with the complex molybdates than with the complex tungstates. The disodium citrates behaved similarly.

Gernez' view that tartaric acid and malic acid form various complexes with sodium molybdate and sodium tungstate according to the amount of the latter salts present does not hold for the concentrations studied by the authors.

It is very probable that, in the cases examined, the trioxides of molybdenum and of tungsten are respectively united with the carboxyl groups of the organic acids.

The speed of the anion is diminished by the introduction of the trioxide of molybdenum or tungsten.

Mixtures containing normal tungstate (1 mol.) and acid (2 mols.) were also examined; the salts formed undergo decomposition at moderate dilutions.

The malate has the probable formula,

$$NaO\cdot MoO_2\cdot CO_2\cdot CH_2\cdot CH(OH)\cdot CO_2Na,$$

and the tartrate, $NaO\cdot MoO_2\cdot CO_2\cdot CH(OH)\cdot CH(OH)\cdot CO_2Na$.

A. McK.

β-*iso*Malic Acid. GERRIT H. COOPS (*Chem. Centr.*, 1904, ii, 641; from *Chem. Weekblad.*, 1, 535—541).—β-iso*Malic acid*, $OH\cdot CH_2\cdot CH(CO_2H)_2$, obtained by hydrolysing the oily ester, $OH\cdot CH_2\cdot CH(CO_2Et)_2$, produced from ethyl sodiomalonate and ethyl trioxymethylene chloride, is a syrup, decomposing on heating into acrylic acid, and yielding amorphous insoluble *calcium* and *copper* salts. W. D. H.

Symmetrical Ethyl Ketopentadienedicarboxylic Acid. FRITZ STRAUS (*Ber.*, 1904, 37, 3293—3298).—Bromine reacts with a chloroform solution of methyl acetonediacetate (hydrochelidonate; Volhard, Abstr., 1890, 30) yielding *methyl dibromoacetonediacetate*,

$$CO(CHBr\cdot CH_2\cdot CO_2Me)_2,$$

which crystallises from methyl alcohol in colourless prisms melting at 58°. When heated with quinoline, hydrogen bromide is evolved and *methyl ketopentadienedicarboxylate*, $CO(CH\colon CH\cdot CO_2Me)_2$, is formed; this crystallises from ethyl acetate in yellow plates melting at 169—169·5°, and yields a *tetrabromide*, which crystallises in small, colourless needles melting and decomposing at 207°. When exposed to sunlight, either in the dry form or in solution, the yellow ester is transformed into a colourless isomeride, which crystallises from ethyl acetate and melts and decomposes at 240—241°.

Ethyl dibromoacetonediacetate forms colourless needles melting at 48·5—49°; *ethyl ketopentadienedicarboxylate* crystallises in yellow prisms and melts at 49·5—50°; the *tetrabromide* melts at 171—172°. *Ketopentadienedicarboxylic acid*, obtained by the hydrolysis of the ethyl ester with 75 per cent. sulphuric acid, crystallises from water in yellow plates decomposing at 230°.

The ethyl ester combines with hydrogen chloride, yielding a *compound*, $C_{11}H_{16}O_5Cl_2$, which crystallises from alcohol in colourless needles melting at 60—75°. Heating with quinoline eliminates hydrogen chloride from this compound, and the original unsaturated acid is obtained.

An ethereal solution of the ester does not yield a precipitate with

mercuric chloride, and on removal of the mercury an oil is obtained which slowly solidifies. J. J. S.

Behaviour of Formaldehyde towards Various Solvents. KÖRBER (*Chem. Centr.*, 1904, ii, 585—586; from *Pharm. Zeit.*, 49, 608).—When formaldehyde is passed into dry chloroform, which is free from acid, at about 130°, diformaldehyde, $C_2H_4O_2$, separates in flakes and partly sublimes, whilst another form of the aldehyde is left in the mother liquor. The action is enormously increased by exposure to sunlight. Diformaldehyde is readily soluble in a small quantity of water; when left in the chloroform mother liquor, it is only very slowly converted by the action of direct sunlight into a form which is insoluble in water. E. W. W.

Acetylacetone-dioxime from Sorbic Acid. FRANZ FEIST (*Ber.*, 1904, 37, 3316).—Acetylacetonedioxime (Harries and Haga, Abstr., 1899, i, 562) is formed when sorbic acid is heated with a methyl-alcoholic solution of free hydroxylamine for five hours at 100°, and may be isolated by evaporation of the solution under reduced pressure, solution in water, and extraction with ether. The oxime readily reduces Fehling's solution, and hence probably exists as the tautomeric hydroxylamino-oxime, OH·NH·CMe:CH·CMe:N·OH. J. J. S.

Final Products of the Hydrolysis of Starch by Oxalic Acid, with special reference to Dierssen's (Lintner's) "*iso*Maltose." FRITZ GRÜTERS (*Zeit. angew. Chem.*, 1904, 17, 1169—1179).—According to Lintner, maltose is not formed during the hydrolysis of starch by oxalic acid, the products successively formed being amylodextrin, erythrodextrin I, erythrodextrin II_α, erythrodextrin II_β, achroodextrin I, achroodextrin II, *iso*maltose, and dextrose, whilst during the hydrolysis of starch by diastase the products are amylodextrin, erythrodextrin I, achroodextrin I, achroodextrin II, *iso*maltose, and maltose. Since Lintner's arguments for the existence of "*iso*maltose" are largely based on his conclusion that in the hydrolysis of starch by oxalic acid no maltose is produced, but a biose, which forms an osazone with properties corresponding with Fischer's *iso*maltosazone, the author has made a further study of the hydrolysis of starch by oxalic acid.

Lintner's conclusions as to the existence of "*iso*maltose" were confirmed by Dierssen (Abstr., 1903, i, 321). The author agrees with Dierssen that starch, free from sucrose, yields by hydrolysis with oxalic acid traces of *d*-fructose.

Potato starch, which was free from sugar, was hydrolysed by oxalic acid and the product submitted to an exhaustive fractionation by dilute alcohol. It is concluded that "*iso*maltose" with $[\alpha]_D$ 140° (Lintner) was not present, and that the products obtained by Lintner and by Dierssen probably contained a considerable amount of some substance which was not a carbohydrate.

From one of the fractions with $[\alpha]_D$ 155°, a carbohydrate having $[\alpha]_D$ 163° was obtained by further fractionation. It was free from sugar, since no osazone could be formed, and it gave no coloration with iodine.

It is designated as achroodextrin IV or maltodextrin γ (compare Ling and Baker, Trans., 1897, 71, 508). It does not crystallise. It is fermentable by bottom yeast, although not very readily. Its specific rotation is slightly lowered by the action of diastase. Its reducing power R = 61 per cent. maltose.

Lintner and Dierssen's "*iso*maltose" is in no way different from a mixture of maltose and dextrin with a small amount of decomposition products.

The products of the hydrolysis of starch by oxalic acid are, according to the author, achroodextrin I, achroodextrin II, maltodextrin γ, maltose, dextrose (*d*-fructose), whilst with diastase the products are achroodextrin I, maltodextrin α, maltodextrin β, maltose (dextrose).

A. McK.

Carbohydrate with High Molecular Weight from the Roots of Heteropteris Pauciflora. CARL MANNICH (*Chem. Centr.*, 1904, ii, 347; from *Ber. deut. pharm. Ges.*, 14, 302—308).—The carbohydrate, *heteropterin*, $C_6H_{10}O_5,\frac{1}{6}H_2O$, resembles starch in appearance, is extremely hygroscopic, and has a slight, but not sweet, taste. It begins to soften when heated at 140° and becomes viscous at 160°; at 195°, it begins to froth. It dissolves in water, has $[\alpha]_D - 40·98°$ at 20° in 6·068 per cent. aqueous solution, reduces Fehling's solution very slightly, reduces ammoniacal silver solutions when boiled for a short time, and gives a white precipitate with baryta. With phenylhydrazine, it yields only a minute amount of osazone. It does not ferment. When hydrolysed, it yields only lævulose. N. H. J. M.

Acetyl Derivative of Cellulose. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 153350).—The ordinary acetylcellulose is insoluble in alcohol. A soluble acetylcellulose is obtained by the action of acetic anhydride on hydrocellulose in the presence of a large quantity of concentrated sulphuric acid. The concentrated alcoholic solution forms a solid jelly when cold, but becomes liquid on warming. Water precipitates the acetyl compound from its solution in alcohol, acetic acid, or acetone. C. H. D.

Alkylamines containing Fluorine. FRÉDÉRIC SWARTS (*Bull. Acad. Roy. Belg.*, 1903, 6, 762—801).—When heated under pressure at 125—145° with alcoholic ammonia, bromodifluoroethane, $CHF_2·CH_2Br$, is converted into a mixture of two amines, difluoroethylamine and tetrafluorodiethylamine, which can be separated by means of their oxalates or hydrochlorides.

Difluoroethylamine, $CHF_2·CH_2·NH_2$, is a colourless liquid with an ammoniacal odour, boiling at 67·5—67·8° (corr.) under 757 mm. pressure, has a sp. gr. 1·175 at 11·9°, absorbs carbon dioxide, and is miscible with water in all proportions. The *hydrochloride* forms colourless crystals melting at 183°, easily soluble in water, but sparingly so in cold alcohol; the *sulphate* crystallises in plates; the normal *oxalate* forms large, colourless crystals and the *platinichloride* brown crystals. *Difluoroethylurethane*, $CHF_2·CH_2·NH·CO_2Et$, forms colourless platelets melt-

ing at 37·6° and boiling at 184°. *Difluoroethylnitroamine* melts at 22·4° and boils at 111—112°; its *ammonium* salt crystallises in needles melting at 91°, and the sodium salt also forms needles.

Tetrafluorodiethylamine, $NH(CH_2{\cdot}CHF_2)_2$, is a colourless liquid with an odour like acetamide; it boils at 124·4° (corr.) under 755 mm. pressure, has a sp. gr. = 1·304 at 16·5°, and forms a *hydrochloride* crystallising in needles which melt at 171° and are easily soluble in alcohol. The *sulphate* crystallises in prisms. *Tetrafluorodiethylnitrosoamine*, $NO{\cdot}N(CH_2{\cdot}CHF_2)_2$, forms a pale yellow liquid boiling at 178·6°. E. F. A.

The Doubly Linked Carbon Nitrogen System >C:N. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1904, 6, 741—754).—Compounds containing the group ·CH:N· are able to unite with either sodium hydrogen sulphite or hydrogen cyanide. Thus, with sodium hydrogen sulphite, crystalline products are obtained of the type

$$-CH(SO_3Na){\cdot}NH-,$$

which further react with acids or bases just as the hydrogen sulphite compounds of aldehydes and ketones do. Thus, from *iso*amylheptylideneimine, a sparingly soluble *compound*, $C_6H_{13}{\cdot}CH(SO_3Na){\cdot}NH{\cdot}C_5H_{11}$, crystallising in plates, is obtained. *Ethylethylideneimine* (boiling at 48°) combines with hydrogen cyanide forming *a-cyanodiethylamine*, $CH_3{\cdot}CH(CN){\cdot}NHEt$, boiling at 153—154°; *propylpropylideneimine*, prepared from propylamine and propaldehyde and boiling at 101—102°, forms *a-cyanodipropylamine*, $C_2H_5{\cdot}CH(CN){\cdot}NH{\cdot}C_3H_7$, boiling at 176—177°, whilst iso*butylethylideneimine*, which boils at 90—91°, forms iso*butyl-a-cyanoethylamine*, $CH_3{\cdot}CH(CN){\cdot}NH{\cdot}C_4H_9$, which distils at 168—169°. These nitrilimines are hydrolysed by acids to the corresponding carboxylic acids; bases convert them into hydrogen cyanide, aldehyde, and primary amine. *Cyanotrimethylamine*, $NMe_2{\cdot}CH_2{\cdot}CN$, obtained by the action of hydrogen cyanide and formaldehyde on dimethylamine, melts at 139°; *dimethyl-a-cyanoethylamine*, $NMe_2{\cdot}CHMe{\cdot}CN$, melts at 144°, whilst *dimethyl-a-cyano*iso*propylamine*, $NMe_2{\cdot}CMe_2{\cdot}CN$, melts at 152°. E. F. A.

Synthesis of Dimethylaminoethyl Ether. LUDWIG KNORR (*Ber.*, 1904, 37, 3504—3505).—Iodoether and dimethylamine combine together at 150° to form the hydriodide of dimethylaminoethyl ether: $NHMe_2 + I{\cdot}C_2H_4{\cdot}O{\cdot}C_2H_5 = NHIMe_2{\cdot}C_2H_4{\cdot}O{\cdot}C_2H_5$.

The same base may be synthesised by heating an alcoholic solution of chloroethyldimethylamine hydrochloride and sodium ethoxide at 150—160°: $NMe_2{\cdot}CH_2{\cdot}CH_2Cl + NaOEt = NMe_2{\cdot}C_2H_4{\cdot}O{\cdot}C_2H_5 + NaCl$. The product is in both cases identical with the base obtained from methylmorphinemethine, thebaine methiodide, or codeinone methiodide (this vol., i, 916). C. H. D.

Aminoethyl Ether. LUDWIG KNORR (*Ber.*, 1904, 37, 3506—3507).—Bromoethylamine hydrobromide reacts with sodium ethoxide in alcoholic solution at 150°, forming *aminoethyl ether*:

$$NH_2{\cdot}CH_2{\cdot}CH_2Br + NaOEt = NaBr + NH_2{\cdot}C_2H_4{\cdot}OEt.$$

After distilling over barium oxide, the ether boils at 108—109° under 760 mm. pressure, and dissolves readily in water or other solvents; it reacts strongly alkaline, and has a powerful amine-like odour. The salts are readily soluble and crystallise with difficulty. The *aurichloride* separates as an oil, which slowly crystallises. C. H. D.

Betaine Periodide. VL. STANĚK (*Zeit. Zuckerind. Böhm.*, 1904, 28, 578—583. See this vol., ii, 790).

Copper Nickel Salts of some Amino-acids. GIUSEPPE BRUNI and C. FORNARA (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 26—30).—The copper salts of the amino-acids differ from most others in having a bluish-violet colour similar to that of the cuprammonium salts.

The copper salts prepared and examined by the authors were those of glycine, α-alanine, α-amino*iso*butyric acid, leucine, aspartic acid, asparagine, and *o*-, *m*-, and *p*-aminobenzoic acids. Except in the case of the last three acids, the copper salts cannot conveniently be prepared by dissolving copper oxide in the acid, but are readily obtainable by mixing the calculated quantity of copper sulphate solution with a cold solution of barium hydroxide, and adding an excess of the pasty mixture of barium sulphate and cupric hydroxide formed to an aqueous solution of the amino-acid. The copper salts of the aminobenzoic acids have a green colour, the intensity of which increases from the ortho- to the para-derivative, and copper aspartate is azure-blue, tending towards violet; the salts of all the α-amino-fatty acids have the characteristic violet colour, which is scarcely intensified by the addition of ammonia to their aqueous solutions. All these salts resemble the cuprammonium compounds in not yielding precipitates with potassium hydroxide, sodium carbonate, or potassium ferrocyanide, or thiocyanate; hydrogen sulphide or an alkali sulphide precipitates cupric sulphide, but only incompletely, whilst potassium cyanide decolorises the solutions. This behaviour shows that in solutions of these salts copper ions are present only in extremely small quantity, so that even with an excess of reagent it is impossible to exceed the relative solubility product.

The corresponding nickel salts, previously unknown, were prepared by treating a solution of the amino-acid with a paste of nickel hydroxide and barium sulphate. *Nickel aminoacetate*,

$$(C_2H_4O_2N)_2Ni,2H_2O,$$

forms minute, pale blue crystals, moderately soluble in water. *Nickel α-aminopropionate*, $(C_3H_6O_2N)_2Ni,4H_2O$, is very similar to the aminoacetate. The nickel salts of the three aminobenzoic acids are green and practically insoluble in water. The aspartate is also green, but moderately soluble in water, but the asparagine derivative is pale blue and gives a dark blue solution. In solutions of these nickel salts, the concentration of the metallic ions seems to be greater than in solutions of the corresponding copper salts, because they give precipitates with alkali sulphides and also with alkali hydroxides and carbonates; they do not, however, yield precipitates with potassium ferrocyanide or sodium phosphate. The nickel salt of asparagine resembles more

the metallo-ammonium compounds, as it is not precipitated by alkali hydroxides or carbonates, and only incompletely by alkali sulphides.

In order that these salts may exhibit the behaviour of the metallo-ammonium salts, it seems necessary that the amino-group should occupy the α-position.

These salts may have either one of two structures in solution. In the case of the copper derivative of glycine, this may be either $\begin{matrix}CH_2\\ \vert \\ CO_2\end{matrix}\!>\!NH_2\cdot Cu\cdot Cu\cdot NH_2\!<\!\begin{matrix}CH_2\\ \vert \\ CO_2\end{matrix}$ or $\left[\begin{matrix}NH_2\text{—}CH_2\cdot CO_2'\\ Cu\\ NH_2\text{—}CH_2\cdot CO_2'\end{matrix}\right]$, in the latter case, the atom of copper being surrounded by two NH_2 groups and two negative radicles, thus forming a neutral and non-ionising complex. T. H. P.

Hydroxylamines. Felix Haase and Richard Wolffenstein (*Ber.*, 1904, **37**, 3228—3238).—Piperidine oxide and benzyl chloride react in cold ethereal solution, forming benzylpiperidine oxide; on reduction with zinc and hydrochloric acid, this forms benzylpiperidine, of which the *hydrochloride* melts at 178° and the platinichloride at 191—193°. 1-Methylpiperidine oxide forms a picrate melting at 176—178° and a platinichloride melting at 188°. The methiodide is reduced by zinc and hydrochloric acid to 1-methylpiperidine.

Diethylhydroxylamine and carbon disulphide unite to form diethylamine diethyldithiocarbamate, melting at 83° and identical with the product obtained from diethylamine and carbon disulphide.

Dibenzylamine dibenzyldithiocarbamate, prepared from dibenzylhydroxylamine in the same manner, melts at 82·5°. Carbanilinopiperidine oxide, prepared by the interaction of phenylcarbimide and piperidine oxide, melts at 105—106° and forms a p-*nitrophenylhydrazone* melting at 211°. Carbanilinodibenzylhydroxylamine forms a p-*nitrophenylhydrazone*, crystallising in yellow needles from ether and melting at 209°. E. F. A.

Electrolytic Preparation of Potassium Cyanate. Emanuele Paternò and E. Pannain (*Gazzetta*, 1904, **34**, ii, 152—155).—The most favourable conditions for the electrolytic oxidation of potassium cyanide to cyanate are: (1) The concentration of the cyanide to be from 4 to 6 gram-mols. per litre. (2) The presence of 1 gram-mol. of potassium hydroxide per litre. (3) An *E.M.F.* of 4 to 6 volts. (4) An anodic current density of from 1 to 4 amperes per sq. dm. (5) The electrolyte to be mixed by agitating the anode. Under these conditions, and if the electrolysis is sufficiently prolonged, almost the whole of the cyanide is converted into cyanate, part of which crystallises out during the electrolysis. T. H. P.

Oxidation of Thiocyanic Acid and its Salts by Hydrogen Peroxide. Joseph H. Kastle and Claude R. Smith (*Amer. Chem. J.*, 1904, **32**, 376—385).—Kastle and Loevenhart (Abstr., 1903, ii, 415, 537) have shown that ammonium thiocyanate is readily oxidised by hydrogen peroxide with formation of ammonium hydrogen sulphate and hydrogen cyanide. This reaction has now been closely studied.

The influence of small quantities of various oxygen carriers, namely, manganese chloride, manganese dioxide, silver nitrate, potassium chloride, bromide, and iodide, copper sulphate, nitrate, and acetate, ferrous sulphate, mercuric chloride, and platinum black, on the action of hydrogen peroxide on thiocyanic acid and its potassium and barium salts has been determined, and the results are tabulated. It is found that, both in presence and absence of oxygen carriers, thiocyanic acid is more rapidly oxidised than either of its salts, and that the oxidation of both the acid and its salts is greatly accelerated by various substances, particularly by those which effect the decomposition of hydrogen peroxide, such as chrome alum, copper sulphate and nitrate, and ferrous sulphate. Nickel and cobalt salts accelerate the oxidation of thiocyanic acid, but have little influence on the oxidation of the salts. Platinum black, manganese dioxide, and potassium iodide have practically no effect on the rate of oxidation.

The oxidation of thiocyanic acid by hydrogen peroxide takes place according to the following equation: $HCNS + 3H_2O_2 = HCN + H_2SO_4 + 2H_2O$. The reaction was studied by van't Hoff's method and appears to be one of the third order. The oxidation probably takes place in two stages: (1) $HCNS + 2H_2O_2 = HCN + 2H_2O + SO_2$; and (2) $SO_2 + H_2O_2 = H_2SO_4$. The velocity of the reaction was determined both with thiocyanic acid and its potassium salt. The results are tabulated and show that it is possible to obtain fairly constant values for the coefficient of velocity of a reaction of the third order. It has also been observed that a rise of temperature of 10° nearly doubles the velocity of the reaction. E. G.

Action of Nitrous Acid on the Amide of Malonic Acid and its Homologues. I. FLORIAN RATZ (*Monatsh.*, 1904, 25, 687—744. Compare this vol., i, 298).—When warmed with concentrated hydrochloric acid, nitromalonamide is hydrolysed, almost quantitatively, to carbon dioxide, ammonia, formic acid, and hydroxylamine.

The action of bromine on nitromalonamide suspended in water leads to the formation of *bromonitromalonamide*,

$$NH_2{\cdot}CO{\cdot}CBr(NO_2){\cdot}CO{\cdot}NH_2,$$

which crystallises in slender, white needles, melts at 131—132°, is easily soluble in acetone or methyl alcohol, and, when boiled with water, is decomposed with evolution of bromonitromethane. With aqueous silver nitrate solution, in presence of very dilute alkali hydroxides or ammonia, it yields a white precipitate consisting of a mixture of silver cyanate and the silver salt of nitromalonamide. When heated in a sealed tube for half an hour with alcohol, or for a few minutes with alcohol in presence of a trace of sodium acetate or of an alkali hydroxide, bromonitromalonamide yields nitromalonamide, dibromonitroacetamide, and a small amount of ethyl allophanate. The *ammonium* salt of ethyl nitromalonate (Franchimont and Klobbie, Abstr., 1889, 1143) crystallises in yellow, hexagonal plates and melts and decomposes at 152—153°. When heated with aqueous or alcoholic ammonia in a sealed tube at 100°, it is converted into nitroacetamide and urethane. The reaction takes place very slowly, part of the ethyl nitromalonate remaining unchanged after three hours' heating.

When boiled with water and one molecular proportion of ammonia, nitromalonamide yields the same products as when it is boiled with water alone, but when boiled with water in presence of an excess of ammonia ($25NH_3 : C_3H_5O_4N_3$) it yields nitroacetamide and carbamide. Nitroacetamide is isolated as its *ammonium* salt, $C_2H_3O_3N_2 \cdot NH_4$, which crystallises in prismatic needles, melts and decomposes at 146—147°, and evolves hydrogen cyanide on prolonged warming in concentrated aqueous solution. With silver nitrate or lead acetate, the aqueous solution gives precipitates consisting of microscopic, prismatic needles; the green precipitate formed on addition of copper acetate is composed of stellate clusters of crystals; with ferrous and ferric salts, amorphous yellow precipitates are formed; the silver salt, $C_2H_3O_3N_2Ag$, explodes when heated. *Nitroacetamide*, $NO_2 \cdot CH_2 \cdot CO \cdot NH_2$, obtained by treating the silver salt with a slight excess of hydrochloric acid, crystallises in slender needles, decomposes at 97—98°, and is easily soluble in water, acetone, or methyl or ethyl alcohols, less so in chloroform, ether, or benzene; its acid nature is less pronounced than that of nitromalonamide. As when nitromalonamide (1 part) is boiled for 30—45 minutes with water (10 parts) and potassium hydroxide (1·52 parts) the products obtained are nitroacetamide and potassium cyanate, the production of carbamide by the action of aqueous ammonia or nitromalonamide is due probably to the intermediate formation of ammonium cyanate.

When boiled with dilute alkali hydroxides or dilute acids, 1 mol. of nitroacetamide slowly yields ammonia, equivalent to 1 atom of nitrogen. With alkali hydroxides, the hydrolysis is slightly more rapid than is that of cyanic acid. If a normal solution of nitroacetamide, to which 5 mols. of potassium hydroxide have been added, is distilled with a current of steam, 1 atom of nitrogen is evolved as ammonia in 30 minutes. From the distillation residue, when cooled, neutralised, and extracted with ether, there is obtained a complex *substance*, $C_4H_5O_7N_3,\frac{3}{4}H_2O$, which crystallises in needles and melts with evolution of a gas. It is very hygroscopic; the aqueous solution gives a strong acid reaction and liberates carbon dioxide from potassium carbonate, but gives no precipitation with silver nitrate. It is so unstable that it commences to decompose and evolve a gas in a vacuum at the ordinary temperature. The *ammonium* salt,

$$C_4H_2O_7N_3(NH)_3,$$

is a white, crystalline powder; the explosive *silver* salt forms microscopic clusters of yellow crystals and quickly blackens, even in absence of light. If nitroacetamide in $N/2$ solution is heated to 100° and potassium hydroxide, 8 mols., slowly added, methazonic acid is obtained. This acid is also obtained directly from the complex substance.

When warmed with concentrated hydrochloric acid, nitroacetamide is hydrolysed, more easily than nitromalonamide, to ammonia, carbon dioxide, formic acid, hydroxylamine, and a trace of oxalic acid.

Dibromonitroacetamide, $NO_2 \cdot CBr_2 \cdot CO \cdot NH_2$, formed by the action of bromine on nitroacetamide in aqueous solution, crystallises from hot water in long needles, from benzene in glistening, fatty leaflets, and is easily soluble in methyl or ethyl alcohol, acetone, or ether. The dibromo-compound is partly decomposed on prolonged boiling with

absolute alcohol, the decomposition being greatly accelerated by the presence of a trace of an alkali hydroxide or of sodium acetate. When triturated with water and treated with potassium hydroxide or ammonia, dibromonitroacetamide yields an oil which has a suffocating odour, is volatile in a current of steam, and gives analytical results corresponding with a mixture of tribromonitro- and dibromonitromethane. The dibromonitromethane at first formed is further brominated, probably at the expense of unchanged dibromonitroacetamide.

Bromonitroacetamide, $NO_2\cdot CHBr\cdot CO\cdot NH_2$, is formed by the action of potassium hydroxide (not more than $1\frac{1}{2}$ mols.) on the dibromo-compound in very dilute solution and in presence of a bromine-absorbent such as carbamide, and treatment of the resulting *potassium* salt, $C_2H_2O_3N_2BrK$, with dilute sulphuric acid. It crystallises in white needles, melts at 79°, and contains a small amount of nitroacetamide.

The action of methyl iodide on silver nitroacetamide, suspended in methyl alcohol, leads to the formation of :

(1) A small amount of nitromethylacetamide, $C_2H_3O_3N_2Me$, which crystallises in long, white needles, melts and decomposes at 112°, and loses half its nitrogen as ammonia when boiled with dilute aqueous alkali hydroxides, but much more slowly than does nitroacetamide. If boiled with dilute sulphuric acid and thereafter distilled with excess of potassium hydroxide, it further loses 21 per cent. of the remaining nitrogen. The small yield of the methyl derivative might be due to the silver salt of nitroacetamide being a mixture of the salts of two stereoisomeric *iso*nitro-compounds. To test this, ammonium nitroacetamide in aqueous solution was precipitated in eleven fractions by silver nitrate. The first fractions were white, the later yellow; both the white and the yellow fractions have the composition $C_2H_3O_3N_2Ag$; the solubility of the white salt is 1 part in 306 of water, that of the yellow salt is 1 part in 151 of water. Both salts give the same nitroacetamide on treatment with hydrochloric acid.

(2) The second *product* from the methylation of silver nitroacetamide is a crystalline substance which melts and decomposes at 250—255°, is only sparingly soluble in boiling methyl or ethyl alcohol, and, when treated with potassium hydroxide in aqueous solution, loses 25 per cent. of its nitrogen as ammonia and yields the *potassium* salt of an acid. This salt is almost insoluble in alcohol; the *silver* salt, $C_4H_4O_5N_3Ag$, crystallises in needles and explodes when heated. The *acid*, $C_4H_5O_5N_3$, obtained from the silver salt by the action of hydrochloric acid, crystallises in small, compact nodules, melts and decomposes at 101°, is easily soluble in water or alcohol, and forms characteristic crystalline insoluble salts with *silver*, *lead*, *copper*, *barium*, and *potassium*.

When reduced with tin and hydrochloric acid, ammonium nitroacetamide yields ammonium chloride and a white, hygroscopic, crystalline *substance* which reduces Fehling's solution at the ordinary temperature and, with copper acetate, forms a precipitate consisting of slender needles. No aminoacetic acid could be detected amongst the products. Even after energetic reduction with excess of tin and hydrochloric acid, and by warming with stannous chloride and hydrochloric acid, no trace of

methylamine and not more than 1 mol. of ammonia per mol. of nitroacetamide could be detected. G. Y.

Solubility and Polymerisation of Cyanogen. Reactions between Cyanogen and Potassium Cyanide. Thermochemical Studies on the Solution and Polymerisation of Cyanogen. The Slow Oxidation of Cyanogen and Cyanides by Free Oxygen. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1904, [viii], 3, 145—181).—A *résumé* of work already published (compare this vol., i, 720, 721, 793). M. A. W.

Preparation of Cyanides from Ferrocyanides. GROSSMANN'S CYANIDE PATENTS SYNDICATE (D.R.-P. 153358. Compare this vol., i, 562).—In the regeneration of potassium ferrocyanide from "Everitt's salt," obtained as a by-product in the preparation of hydrocyanic acid from ferrocyanides, alkali carbonate may replace the alkali hydroxide. Little more than the theoretical quantity of alkali carbonate is required, and on passing a current of air the iron is precipitated as ferric hydroxide. C. H. D.

A Reaction of Potassium Ferrocyanide. ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1904, 41, 61—62).—When an aqueous solution of potassium ferrocyanide is warmed with a freshly-prepared aqueous solution of phenylhydrazine hydrochloride, the liquid assumes first a brownish-red and then a bright red colour. It finally becomes dark red, and a yellowish-green residue separates with evolution of nitrogen and hydrogen cyanide. When submitted to steam distillation, the product yields a dark oil, which crystallises to a red mass, melting at about 45°. When concentrated sulphuric acid is added, the product becomes bright green and then brown. A. McK.

1 : 3-Dimethyl*cyclo*hexane derived from Camphoric Acid. LUIGI BALBIANO and L. ANGELONI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 142—148).—The reduction of camphoric acid by means of phosphorus and hydriodic acid yields 1 : 3-dimethyl*cyclo*hexane (Zelinsky, Abstr., 1895, i, 411), which, on oxidation with nitric acid, gives trinitro-*m*-xylene and formic and glutaric acids. The reduction of the camphoric acid takes place according to the following scheme:

$$CO_2H\cdot CMe<\begin{matrix}CMe_2\cdot CH\cdot CO_2H\\ |\\ CH_2-CH_2\end{matrix} \longrightarrow CHMe<\begin{matrix}CMe_2\cdot CH_2\\ |\\ CH_2-CH_2\end{matrix}$$

$$\longrightarrow CHMe<\begin{matrix}CH_2\cdot CHMe\\ CH_2-CH_2\end{matrix}>CH_2.$$

T. H. P.

Preparation of Benzene and its Homologues from Russian Naphtha by Nikiforoff's Method. W. N. OGLOBLIN (*Zeit. Farb. Text. Ind.*, 1904, 3, 293—294. Compare this vol., i, 729).—The naphtha is first passed, under the ordinary pressure, through retorts heated at 525—550°, and the distillate obtained heated at 1200° under a pressure of two atmospheres. Every 100 grams of the naphtha gives, under this treatment, 38·9 grams of "grey benzene," which

consists of a mixture of 5·59 grams of benzene, 4·00 of toluene, and 2·11 of xylene; after fractionation, 4·56 grams of pure benzene are obtained. The fact that the product contains neither acids nor bases renders its purification easy, and makes this method of preparation of benzene and its homologues preferable to that involving the distillation of coal-tar. W. A. D.

Ozobenzene. CARL D. HARRIES and VALENTIN WEISS (*Ber.*, 1904, 37, 3431—3433. Compare Renard, Abstr., 1895, i, 593; this vol., i, 361).—Ozobenzene, $C_6H_6O_9$, is formed as an opalescent, gelatinous mass when a current of ozone is passed through benzene for 1—2 hours at 5—10°. Commercial benzene, which is free from thiophen and has been distilled over sodium, forms ozobenzene. On evaporation of the excess of benzene, the product is obtained as a white, amorphous, highly explosive mass, which, on treatment with water at 0°, is converted into an even more explosive crystalline modification. Not more than 0·1 gram of ozobenzene should be prepared at one time. Under reduced pressure, or in a current of air, it gradually volatilises; it is sparingly soluble, or insoluble, in the ordinary solvents. When carefully warmed with water, ozobenzene yields glyoxal, which is identified by conversion into its osazone. Ozobenzene, or benzenetriozonide, is represented by the formula

$$O_3{<}\begin{array}{c} O_3 \\ \diagup\diagdown \\ CH{\cdot}CH{\cdot}CH \\ | \qquad\quad | \\ CH{\cdot}CH{\cdot}CH \\ \diagdown\diagup \\ O_3 \end{array}.$$

G. Y.

Certain Derivatives of 1 : 3 : 5-Tri-iodo-2 : 4-dinitrobenzene. C. LORING JACKSON and J. F. LANGMAID (*Amer. Chem. J.*, 1904, 32, 297—308).—When 1 : 3 : 5-tri-iodo-2 : 4-dinitrobenzene is boiled with sodium methoxide, it is converted into *tri-iodonitroanisole*,

$$NO_2{\cdot}C_6HI_3{\cdot}OMe,$$

which crystallises from alcohol in white or very pale yellow, slender prisms, melts at 128°, and is soluble in benzene, ether, chloroform, acetone, carbon disulphide, or acetic acid; a small quantity of a crystalline *substance* [possibly $NO_2{\cdot}C_6HI(OMe)_3$], which melts at 253—256°, is also produced in this reaction.

By the action of sodium ethoxide on tri-iododinitrobenzene, a compound is obtained which melts at 130° and is probably identical with the dinitroresorcinol diethyl ether described by Jackson and Warren (Abstr., 1891, 1025); a small quantity of another substance is produced which crystallises in plates and melts at about 200°.

When tri-iododinitrobenzene is treated with ethyl sodiomalonate, di-iododinitrobenzene, ethyl iododinitrophenylmalonate, an additive compound of di-iododinitrobenzene and tri-iododinitrobenzene, and a substance which melts at 73° and does not contain iodine are obtained. The di-iododinitrobenzene melts at 160° and is probably identical with the compound prepared by Istrati and Georgescu (Abstr., 1892, 1310) by the action of nitric acid on tri-iodobenzene. *Ethyl iododinitrophenylmalonate*, $C_6H_2I(NO_2)_2{\cdot}CH(CO_2Et)_2$, crystallises from alcohol in

yellow, rhombic plates, melts at 83°, and is soluble in ether, benzene, chloroform, acetone, glacial acetic acid, or carbon disulphide. The additive *compound*, $2C_6H_2I_2(NO_2)_2,C_6I_3(NO_2)_3$, crystallises from alcohol in pale yellow, long, slender prisms, melts at 182°, and is soluble in benzene, ether, chloroform, acetone, or carbon disulphide. E. G.

Action of Magnesium Ethyl Iodide on Nitrobenzene. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 220—224). The action of magnesium ethyl iodide on nitrobenzene in ethereal solution yields a *compound*, O:NPhEt·O·MgI, which with pyridine gives an *additive compound*, $C_8H_{10}O_2IMg,C_5H_5N$. The action of water on the first compound yields ethylaniline as the principal product.

T. H. P.

A Chloro-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 153195).—A *chloro*-1 : 8-*dihydroxynaphthalene*-3 : 6-*disulphonic acid*, prepared by the action of alkaline hypochlorite solutions on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromotropic acid), separates from dilute sodium chloride solution in colourless crystals and combines readily with diazonium salts. C. H. D.

Action of Acetylene on Magnesium Phenyl Bromide. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 187—193).—It has been shown by Jocitsch (*Bull. Soc. chim.*, 1902, [iii], 28, 208) that on passing acetylene into an ethereal solution of magnesium methylbromide, ethane and the compound, BrMg·C:C·MgBr, are formed :

$$CH:CH + 2EtMgBr = BrMg·C:C·MgBr + C_2H_6,$$

whilst with the higher homologues of acetylene the action is :

$$CR:CH + EtMgBr = CR:C·MgBr + C_2H_6.$$

The magnesio-acetylene derivatives thus obtained resemble, in their behaviour, the compounds prepared by Grignard (Abstr., 1901, i, 263) ; thus, with water they yield the corresponding acetylenic hydrocarbon, with ketones they give tertiary acetylenic alcohols, and with aldehydes secondary acetylenic alcohols. All these compounds have the ·C:C· group arranged between two carbon atoms. The compounds prepared by the author are described below.

Magnesio-acetylene bromide, HC:C·MgBr, prepared by passing acetylene into the ethereal solution obtained by the action of powdered magnesium and iodine on an ethereal solution of bromobenzene, forms an oily liquid, which undergoes change in moist air and gives a vigorous evolution of acetylene when treated with water. With pyridine in ethereal solution, it yields the *compound* $HC:C·MgBr,C_5H_5N,Et_2O$ as a yellow precipitate. With benzaldehyde, it gives : (1) a *hydrocarbon*, $C_{18}H_{14}$, which separates from light petroleum in white, nacreous crystals melting at 213—214°, and soluble in benzene, chloroform, or carbon disulphide and to a slight extent in alcohol, ether, or light petroleum ; it dissolves in boiling nitric acid, which, on cooling, deposits needles which do not melt at 270°. (2) The *ether* of *phenylacetylenecarbinol*, CH:C·CHPh·O·CHPh·C:CH, which boils at 155—160° under 10 mm. pressure. (3) A liquid boiling at 196—200° and having a composition

agreeing well with the formula $C_{18}H_{14}O$. The two latter compounds are being further investigated. T. H. P.

Electrolytic Oxidation of Anthracene. A. FONTANA and FREDERICK M. PERKIN (*Chem. Centr.*, 1904, ii, 708—709; from *Elektrochem. Zeit.*, 11, 99—105).—One hundred grams of acetone dissolve 1·053 of anthracene at 21° and 1·664 at 36°, whilst the solubility of anthraquinone is 0·536 at 20° and 0·812 at 36°. For the purpose of electrolytic oxidation, 10 grams of anthracene are dissolved in a mixture of 550 c.c. of acetone and 100 c.c. of a 40 per cent. solution of sulphuric acid. The solution becomes clear on warming, but the presence of undissolved anthracene is not disadvantageous since, as the quinone is formed, more anthracene is dissolved. The oxidation was effected at about 40° in a glass cell with platinum electrodes, using a current density of 1—3 amperes per sq. dcm. The anode rotated between two cathodes which were contained in porous cells. When a leaden vessel is used for the anode compartment, the product has a dark colour. A yield of 55 per cent. was obtained; in alkaline solution, the yield is less. Yields of up to 80 per cent. may be obtained by adding oxygen carriers, without using special solvents, but employing the anthracene in fine suspension. Experiments with chromium compounds (chromate or chrome alum), manganese in acid or alkaline solutions (manganese sulphate or potassium permanganate), and cerium sulphate are described in the original paper. In most cases, the product consisted of dark yellow crystals, but pale yellow crystals were obtained when an acid solution of a manganese salt was added. By using a comparatively small cathode surface and a large anode, the same results may be practically obtained without employing a diaphragm, but the process is somewhat slower. E. W. W.

Researches in the Phenanthrene Series. ALFRED WERNER (*Ber.*, 1904, **37**, 3083—3088).—A reply to certain criticisms by Schmidt (this vol., i, 69—71) of the author's earlier work.

W. A. D.

β-Dibromophenanthrene. ALFRED WERNER and A. EGGER (*Ber.*, 1904, **37**, 3026—3030. Compare Abstr., 1902, i, 437).—The action of bromine on phenanthrene in carbon disulphide solution leads to the formation of a dibromophenanthrene, $C_{14}H_8Br_2$, which crystallises in long, white needles, melts at 146°, and is probably identical with Zetter's α-dibromophenanthrene (Abstr., 1878, 510). Zetter's supposed β-dibromophenanthrene (*loc. cit.*), obtained by bromination of phenanthrene in ethereal solution, is identical with Fittig and Schmitz's dibromofluorene (*Annalen*, 1878, **193**, 137), which crystallises from ether in leaflets, from benzene in triclinic plates, melts at 164°, and is oxidised by chromic acid in glacial acetic acid solution to Holm's β-dibromofluorenone (Abstr., 1883, 921), which melts at 202°.

G. Y.

Derivatives of Triphenylmethane. EMIL FISCHER and OTTO FISCHER (*Ber.*, 1904, **37**, 3355—3360).—The authors found (*Annalen*,

1878, 194, 242) that when trinitrotriphenylmethane in glacial acetic acid solution is oxidised by chromic acid, the melting point of the carbinol formed is 171—172°. O. Fischer and G. Schmidt (*Zeit. Farb. Text. Ind.*, 3, 1) have since found that when the oxidation is conducted in alkaline solution with oxygen, the carbinol formed melts at 188—189°, this being identical with the figure obtained by Gomberg (this vol., i, 490), who oxidised trinitrotriphenylmethane at 100° with chromic acid. The cause of this variation in the melting point of trinitrotriphenylcarbinol has now been studied.

When the product obtained by the oxidation with chromic acid is repeatedly crystallised from benzene or glacial acetic acid, the carbinol melting at 188—189° is obtained. With one crystallisation of the crude product, however, the melting point varies between 165° and 170°. Trinitrotriphenylcarbinol exhibits dimorphism. The one form, melting at 189°, is monoclinic. The other form is obtained by oxidising trinitrotriphenylmethane by air at 0°; the benzene layer remaining after shaking out the alcohol with water is then quickly evaporated, the residue dissolved in cold ethyl acetate, and the crystallisation accelerated by the addition of light petroleum. When the solution is allowed to crystallise slowly, iridescent crystals of the rhombic form, melting at 167°, separate. These crystals lose their lustre after several days; they do not, however, lose weight in so doing, but the melting point rises from 4° to 5°. The rhombic form, accordingly, is the unstable variety, which is gradually transformed into the stable monoclinic form.

The crude hydrocarbon, obtained by the oxidation of leucaniline, was mixed with a trace of diphenyl-*m*-tolylmethane (compare Bistrzycki and Gyr, this vol., i, 315). The crystals which separated melted at 60—61°, and when oxidised yielded the carbinol, melting at 68—69°; the mother liquor from which the crystals had been removed yielded a product melting at 62—67°, which, when oxidised, formed the carbinol melting at 150°.

In the transformation of leucaniline into diphenyltolylmethane, an excess of strong sulphuric acid and of nitrous fumes should be avoided by decomposing the diazo-compound slowly.

When diphenyl-*m*-tolylmethane (m. p. 61—62°) is oxidised by chromic acid, the corresponding carbinol and an oil, which is probably phenyl-*m*-tolyl ketone, are formed. A. McK.

9:10-Diphenylphenanthrene, a Product of Intramolecular Rearrangement. ALFRED WERNER and ARMIN GROB (*Ber.*, 1904, 37, 2887—2903).—Fluorene alcohol (diphenylcarbinol),

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH{\cdot}OH,$$

is best prepared by reducing fluorenone (diphenylene ketone) with zinc dust. Phosphorus pentachloride converts it into *diphenylenechloromethane*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CHCl$, crystallising from alcohol in long, colourless needles and melting at 90°. The chloro-compound reacts with benzene and aluminium chloride, and after decomposing with water and

distilling the benzene layer, phenylfluorene (phenyldiphenylene-methane), $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!\!>\!CHPh$, is obtained, melting at 146—148° (compare Hanriot and St. Pierre, Abstr., 1889, 882). Phenylfluorene dissolves potassium at 240—280°, and the product reacts with benzoyl chloride on boiling, forming benzoylphenylfluorene, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!\!>\!CHPh{\cdot}COPh$, which is identical with the compound obtained from triphenylmethane by Hanriot and St. Pierre. Distillation with zinc dust or heating with alcoholic potassium hydroxide at 200° regenerates the phenylfluorene. Hydriodic acid and red phosphorus under pressure reduce the benzoyl compound to diphenylphenanthrene.

o-Dibenzoyldiphenyl, $COPh{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}COPh$, prepared by heating *o*-bromobenzophenone with copper powder at 260—360°, crystallises in prisms and melts at 165—167° (compare Klinger and Lonnes, Abstr., 1896, i, 691). When distilled with zinc dust, 9 : 10-*diphenylphenanthrene*, $\begin{matrix}C_6H_4{\cdot}CPh\\ | \quad\quad || \\ C_6H_4{\cdot}CPh\end{matrix}$, is obtained, crystallising in colourless needles and melting at 233—234°. Chromic acid oxidises it again to the dibenzoyl compound.

Zinc and potassium hydroxide reduce *o*-dibenzoyldiphenyl to a *pinacone*, $C_{26}H_{20}O_2$, crystallising from alcohol in small, white needles and melting at 202—204°. Hydriodic acid and red phosphorus reduce it to 9 : 10-diphenylphenanthrene.

Phenanthraquinone and magnesium phenyl iodide react to form a pinacone, *dihydroxydiphenyldihydrophenanthrene*, $\begin{matrix}C_6H_4{\cdot}CPh{\cdot}OH\\ | \quad\quad | \\ C_6H_4{\cdot}CPh{\cdot}OH\end{matrix}$, separating from water in colourless crystals and melting at 178—179°. This compound appears to be stereoisomeric with the above-named pinacone. It yields 9 : 10-diphenylphenanthrene on distillation with zinc dust. Both pinacones yield *o*-dibenzoyldiphenyl on oxidation with chromic acid, and form the same *anhydride*, $C_{26}H_{18}O$, on heating with hydrochloric and sulphuric acids at 200—220°. The anhydride crystallises from alcohol in rhombic prisms and melts at 194—196°. It yields 9 : 10-diphenylphenanthrene on distillation with zinc dust.

C. H. D.

The Anthracene Series. Dibenzylanthracene and its Derivatives. EDUARD LIPPMANN and RODOLFO FRITSCH (*Monatsh.*, 1904, 25, 793—807. Compare Abstr., 1902, i, 754).—When pure, bromodibenzylanthracene melts, if rapidly heated, at 187°, without decomposing.

Dibenzylideneanthracene, $C_6H_4\!<\!\begin{matrix}C\text{———}\\ | \!>\!C_6H_4\\ C\text{———}\end{matrix}\begin{matrix}CHPh\\ | \\ CHPh\end{matrix}$, is prepared by heating bromodibenzylanthracene with acetic anhydride; it is also formed when the bromine compound is heated at 125—130°, or boiled with dilute potassium carbonate solution, or heated with glacial acetic acid, or with a benzene solution of quinoline (2 mols.). It is precipitated, on addition of alcohol to its solution in chloroform, in yellow crystals

and melts at 234—236° (some preparations melted at 237—240°). The action of bromine on dibenzylideneanthracene in chloroform solution leads to the evolution of hydrogen bromide and the formation of a residue containing bromine; when boiled with xylene, the residue loses bromine and yields a *product* which melts at 243°; if boiled with glacial acetic acid, the residue forms a *substance* which is free from bromine, melts at 199°, and yields potassium acetate when hydrolysed with potassium hydroxide.

If bromodibenzylanthracene is boiled with aqueous potassium or lead acetate, the product is a mixture of dibenzylideneanthracene and bisdibenzylideneanthracene, which is the main product if the bromine compound is boiled with 1 mol. of quinoline in benzene solution for ten hours before the addition of a second molecular proportion of quinoline.

Bisdibenzylideneanthracene,

$$C_6H_4<\begin{matrix}C\\|\\C\end{matrix}>C_6H_4\begin{matrix}\text{—CHPh·CHPh—}\\ \\ \text{—CHPh·CHPh—}\end{matrix}C_6H_4<\begin{matrix}C\\|\\C\end{matrix}>C_6H_4,$$

forms compact, yellow crystals, melts at 184°, dissolves in chloroform to a red, fluorescent solution, and gives a green coloration with concentrated sulphuric acid.

The action of aniline on bromodibenzylanthracene in chloroform solution leads to the formation of *anilinodibenzylanthracene*,

$$NHPh\cdot CHPh\cdot C<\begin{matrix}C_6H_4\\ \\ C_6H_4\end{matrix}>C\cdot CH_2Ph \text{ or } C_6H_4<\begin{matrix}C\\|\\C\end{matrix}>C_6H_4\begin{matrix}\text{—CHPh}\\ \\ \text{—CHPh}\end{matrix}>NPh,$$

which is obtained in yellowish-green crystals and melts at 233°. The ethoxy-derivative, obtained by the action of alcohol on the bromine compound in boiling benzene solution, forms crystals containing 1 mol. of benzene, which melt at 217°, lose C_6H_6 at 178°, and then melt at 197°. When boiled with dilute sulphuric acid, the ethoxy-derivative yields the *ether*, $C_{28}H_{21}\cdot O\cdot C_{28}H_{21}$, which crystallises in white scales and melts at 213—215°. *Acetoxydibenzylanthracene*, formed by the action of silver acetate on the bromine compound in chloroform solution, melts at 158° and is hydrolysed by alcoholic potassium hydroxide to *hydroxydibenzylanthracene*, $CH_2Ph\cdot C_{14}H_8\cdot CHPh\cdot OH$, which forms flesh-coloured crystals and melts at 151°. G. Y.

Glycerol Derivatives of Aromatic Bases. PAUL COHN and PAUL FRIEDLÄNDER (*Ber.*, 1904, 37, 3034—3036).—*p*-Toluidine combines with epichlorohydrin to form a compound, $C_{10}H_{14}ONCl$, crystallising in colourless needles from benzene and melting at 81—82°. When heated with sodium ethoxide, this is converted into the compound $C_7H_7\cdot NH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OEt$, forming colourless needles and melting at 41—42°. On heating with 2 molecules of toluidine, epichlorohydrin forms the compound $C_{17}H_{22}ON_2$, melting at 113·5°. This gives a *dinitrosoamine* crystallising in yellowish-white needles melting at 223°; the corresponding *nitrosoamine* of the monotoluidine product melts at 70·5°. E. F. A.

Spatial Configuration of Tervalent Nitrogen Compounds. HUMPHREY O. JONES and J. P. MILLINGTON (*Proc. Camb. Phil. Soc.*, 1904, 12, [vi], 489—492).—The authors have made experiments on

the resolution of nitrogen compounds of the type $NR^1R^{11}R^{111}$ by methods which would not involve a change in the active valency of the nitrogen atom (compare Kipping and Salway, Trans., 1904, 85, 438).

α-Phenylbenzylhydrazine gave a *d*-camphorsulphonate forming prisms melting at 156—157°, and having $[M]_D$ in 2 per cent. solution +53—54°. No resolution of the base was obtained.

Methylethylaniline, on sulphonation, yields *methylethylanilinesulphonic acid* melting at 249—250°, easily soluble in water, less readily in alcohol, and forming a *barium* salt crystallising with $2H_2O$. The *brucine* salt, $C_{32}H_{39}O_7N_3S,4H_2O$, forms lustrous prisms soluble to the extent of about 1 per cent. in water, and sparingly soluble in organic solvents. After dehydration, it melts at about 90°. It gives $[M]_D$ −120°, no alteration, indicating a resolution, being obtained on fractional crystallisation. G. D. L.

Preparation of Salts of Dialkylaminomethanesulphonic Acids. Emil Knoevenagel (D.R.-P. 153193).—The alkali hydrogen sulphite compounds of formaldehyde (hydroxymethanesulphonates) react with secondary amines forming dialkylaminomethanesulphonates. Thus formaldehyde, sodium hydrogen sulphite, and methylaniline combine on warming to form *sodium phenylmethylaminomethanesulphonate*, $NPhMe\cdot CH_2\cdot SO_3Na$. Ethylaniline, benzylaniline, diethylamine, and piperidine react in similar manner. The sulphonates crystallise from water or dilute alcohol and are hydrolysed by heating with alkalis. Metallic cyanides convert them into dialkylaminoacetonitriles.

C. H. D.

***N*-α-Naphthylhydroxylamine.** Johannes Scheiber (*Ber.*, 1904, 37, 3055—3057).—In contradistinction to Wacker's observations (Abstr., 1901, i, 655), naphthylhydroxylamine melts at 78—79°, crystallises in faintly yellow, glistening plates, and has the composition $C_{10}H_{11}O_2N$. E. F. A.

Hydrolysis of Dipeptides with Pancreas Ferment. Emil Fischer and Peter Bergell (*Ber.*, 1904, 37, 3103—3108. Compare Abstr., 1903, i, 694).—Under the influence of trypsin glycyl-*l*-tyrosine is converted into *l*-tyrosine and glycine, about 50—55 per cent. of the theoretical quantity of tyrosine crystallising from solution. The racemic form of *leucylalanine*, which melts and decomposes at 245°, is resolved into leucyl-*d*-alanine and an active dipeptide, probably leucyl-*l*-alanine. Similarly, alanyl-leucine and leucyl-leucine were resolved into an active dipeptide and two amino-acids. Hydrolysis is very incomplete in these three cases and the authors emphasise the importance of working with fresh pancreatic secretions. E. F. A.

Syntheses of Polypeptides. VI. Derivatives of Phenylalanine. Hermann Leuchs and Umetaro Suzuki (*Ber.*, 1904, 37, 3306—3315. Compare Abstr., 1903, i, 465, 607, 799; this vol., i, 652, 771, 890).—*α-Bromoisohexoylphenylalanine*,

$$C_4H_9\cdot CHBr\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2Ph,$$

obtained by the action of α-bromohexoyl chloride on phenylalanine in the presence of alkali, crystallises from toluene in colourless, double, six-sided pyramids. It melts at 119—123° (corr.) and is readily soluble in most organic solvents with the exception of benzene, toluene, and light petroleum. That it is a mixture of two stereoisomerides is proved by the action of ammonia at 100°, when α- and *β leucylphenylalanines*, $C_4H_9 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2Ph$, are obtained. The α-compound crystallises from dilute alcohol in minute prisms containing $1H_2O$, which it loses at 105—110°. It melts at 220—223° (corr.), is readily soluble in hot water, but practically insoluble in the usual organic solvents. Its aqueous solution has an acid reaction and it dissolves in both alkalis and acids. Its faintly acidified solution gives a copious precipitate with phosphotungstic acid, but this dissolves either on warming or in the presence of a large excess of mineral acid. Its *phenylcarbimide* derivative,

$$NHPh \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2Ph,$$

crystallises in six-sided, rhombic plates, melts and decomposes at 193—195° (corr.), and dissolves fairly readily in alcohol, ether, ethyl acetate, or acetone.

The *hydrochloride* of the *ethyl ester* of α-leucylphenylalanine,

$$NH_3Cl \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH(CO_2Et) \cdot CH_2Ph,$$

obtained by warming the α-compound for a short time with an alcoholic solution of hydrogen chloride, crystallises from hot alcohol in minute, four-sided plates, melts and decomposes at 193—195° (corr.), and is readily soluble in water. The α-compound reacts with ethyl chlorocarbonate yielding *carbethoxy-α-leucylphenylalanine*,

$$CO_2Et \cdot NH \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2Ph,$$

which crystallises in needles, melts at 140—141·5° (corr.), and is readily soluble in alcohol or ether.

β-Leucylphenylalanine is insoluble in dilute alcohol, is anhydrous, and melts and decomposes when quickly heated at 259° (corr.). Its *phenylcarbimide* derivative crystallises in small needles and melts and decomposes at 183—184° (corr.).

*α-Bromo*iso*hexoyl-α-leucylphenylalanine*,

$$C_4H_9 \cdot CHBr \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2Ph,$$

obtained by the action of α-bromo*iso*hexoyl chloride on α-leucylphenylalanine, crystallises from benzene in colourless needles, melts at 163—165° (corr.), and dissolves readily in chloroform. When heated with aqueous ammonia at 100°, it yields *leucyl-α-leucylphenylalanine*,

$$NH_2 \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH(C_4H_9) \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2Ph,$$

which crystallises from 80 per cent. alcohol with $2H_2O$, and melts at 225—227° (corr.) to a colourless oil.

α-Bromopropionylphenylalanine,

$$CHMeBr \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2Ph,$$

crystallises from benzene in colourless needles, melts at 132—133° (corr.), and is readily soluble in most organic solvents. Ammonia converts it into *alanylphenylalanine*,

$$NH_2 \cdot CHMe \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2Ph,$$

which is precipitated from its aqueous solutions, on the addition of

alcohol, in the form of short prisms containing $2H_2O$ and decomposing and melting at 241—243° (corr.).

Chloroacetylphenylalanine, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph$, melts at 130—131° (corr.) and crystallises from water in four-sided plates. With ammonia, it yields *glycylphenylalanine*,

$$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph,$$

which melts and decomposes at 270° when rapidly heated.

a-Bromoisohexoylglycylphenylalanine,

$$C_4H_9{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph,$$

melts at 163—164° (corr.) and is insoluble in benzene, light petroleum, or water. *Leucylglycylphenylalanine*,

$$C_4H_9{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph,$$

melts and decomposes at 225—228° (corr.).

Chloroacetylglycylphenylalanine melts at 151—152° and with ammonia yields *diglycylphenylalanine*,

$$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2Ph,$$

which melts and decomposes at 238—239° (corr.). It dissolves readily in hot water and crystallises in long needles. With cupric salts and alkali, it gives a bluish-violet coloration.

J. J. S.

Study and Synthetical Preparation of some *s*-Arylthiocarbamides. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1904, **139**, 450—451).—The author obtains a quantitative yield of the *s*-arylthiocarbamide by heating the corresponding aromatic amine in alcoholic solution with excess of carbon disulphide in the presence of potassium hydroxide, according to the following equation :

$$2RNH_2 + CS_2 = CS(NHR)_2 + H_2S$$

(compare, however, Weith, *Ber.*, 1873, **6**, 967). No new compounds are described.

M. A. W.

***p*-Tolyltaurine.** HANS WOLFBAUER (*Monatsh.*, 1904, **25**, 682—686).—When oxidised with potassium chlorate and fuming hydrochloric acid (compare Andreasch, Abstr., 1883, 664), 2-*p*-tolylimino-3-*p*-tolyldihydrothiazoline yields the *anhydride* of di-*p*-tolyltaurocarbamic acid, $CO{<}{\substack{N(C_7H_7){-}SO_2\\ N(C_7H_7){\cdot}CH_2}}{>}CH_2$, which crystallises in glistening leaflets, melts at 204°, and is insoluble in water, but moderately soluble in boiling alcohol or glacial acetic acid. When boiled with baryta in aqueous solution, the anhydride yields carbon dioxide, *p*-toluidine, and the *barium* salt of *p*-tolyltaurine, $(C_9H_{12}O_3NS)_2Ba$, which crystallises in glistening leaflets.

p-*Tolyltaurine*, $C_7H_7{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$, crystallises in thin leaflets or plates, melts and decomposes at 254°, is easily soluble in water, alcohol, or glacial acetic acid, but only slightly so in ether, and gives a strongly acid reaction, decomposing carbonates with evolution of carbon dioxide.

G. Y.

[Aminotolylthiocarbamide.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 152027).—On adding potassium thiocyanate

to a solution of tolylene-2 : 4-diamine hydrochloride, the *monothiocyanate* is formed. This is converted on heating at 120° into *aminotolylthiocarbamide*, which forms a greyish-white powder, dissolving sparingly in water or alcohol, more readily in hot acids, and melting at 170°. A yellow dye is obtained on heating it with sulphur at 200—250°. C. H. D.

Picramic Acid (Dinitraminophenol). A. FRÉBAULT and JULES ALOY (*J. Pharm. Chim.*, 1904, [vi], 20, 245—247).—Picramic acid is best prepared by boiling an aqueous or methyl alcoholic solution of picric acid with slight excess of ammonia and zinc powder for half an hour, the liquid being from time to time mixed with a little more ammonia. Picramic acid, unlike picric acid, is not explosive when suddenly heated. It does not precipitate peptones, albumoses, albumin, or alkaloids. With sodium hypobromite, it yields bromopicrin, $CBr_3 \cdot NO_2$.

Estimation of Potassium.—Potassium picrate, obtained in due course by precipitation with sodium picrate in the presence of alcohol, is boiled with sodium carbonate and dextrose, which reduces the picrate to picramate, which is then estimated colorimetrically.

L. DE K.

Preparation of *p*-Aminophenol-*m*-sulphonic Acid. KALLE & Co. (D.R.-P. 153123. Compare this vol., i, 664).—In the former method of preparation of *p*-nitrophenol-*m*-sulphonic acid from *p*-nitroacetylmetanilic acid, nitroresorcinol is obtained as a by-product. This is avoided by boiling the nitroacetylmetanilic acid with concentrated sodium carbonate or dilute sodium hydroxide solution in a reflux apparatus, when the hydrolysis is confined to the acetylamino-group. C. H. D.

The rendering Active of Oxygen. XI. Autoxidation of Thiophenol. CARL ENGLER and H. BRONIATOWSKI (*Ber.*, 1904, 37, 3274—3276).—The autoxidation of thiophenol in potassium carbonate solution, or better, in dilute ammonia, has been investigated in an apparatus similar to that used by Baur (*Zeit. anorg. Chem.*, 1897, 13, 251). The thiophenol is placed in a thin-walled bulb, which can be broken after the reading is taken. The absorption of oxygen is slow and requires some seven days for completion. The results obtained agree with the absorption of one molecule of oxygen for every four molecules of thiophenol. The reaction therefore probably proceeds in the two stages: $2PhSH + O_2 = Ph_2S_2 + H_2O_2$, $2PhSH + H_2O_2 = Ph_2S_2 + 2H_2O$. The presence of hydrogen peroxide has been proved by the aid of titaniumsulphuric acid. J. J. S.

Trinitro-*m*-cresol. ERNST MURMANN (*Chem. Centr.*, 1904, ii, 436; from *Oesterr. Chem. Zeit.*, 7, 273).—The melting point of trinitro-*m*-cresol, which had been purified by repeatedly crystallising from water and chloroform, has been found to be 109·5°. E. W. W.

Symmetrical Trinitroxylenol. EDMUND KNECHT and EVA HIBBERT (*Ber.*, 1904, **37**, 3477—3479).—When Knoevenagel's *s*-xylenol is nitrated by solution in a mixture of concentrated and 20 per cent. fuming sulphuric acid and admixture with concentrated nitric acid, the *trinitro*-derivative, $OH \cdot C_6Me_2(NO_2)_3$ [$Me_2 : OH : (NO_2)_3 =$ 1 : 3 : 5 : 2 : 4 : 6], is obtained. It is soluble in hot water and is best purified by means of its *potassium* salt, which is sparingly soluble in potassium chloride solution. This salt forms long, brownish-yellow crystals, and when boiled with dilute hydrochloric acid yields the free trinitroxylenol, which crystallises from hot water in straw-yellow needles melting at 108°. It is less soluble in water than picric acid, and in the sulphuric acid bath dyes wool a somewhat redder shade than picric acid. It reacts with ammonium sulphide in the same manner as picric acid and trinitrocresol, but is not affected by potassium cyanide.

Potassium dinitroxylenolsulphonate, $OH \cdot C_6Me_2(NO_2)_2 \cdot SO_3K$, is obtained as a by-product in the preparation of the trinitro-compound.

J. J. S.

Action of Nitrous Acid on Brominated Phenols. G. DAHMER (*Annalen*, 1904, **333**, 346—370).—It has been shown by Thiele (Abstr., 1900, i, 500) and Zincke (Abstr., 1900, i, 545) that in the action of nitrous acid on phenols a hydrogen or bromine atom in the ortho-position is replaced by the nitro-group. This reaction has now been more fully investigated.

Of the monobromophenols, only the para-compound yields a single product, namely, 4-bromo-2-nitrophenol (m. p. 89—90°).

Both 2-bromo- and 2 : 6-dibromothymol ($Me : Pr : OH : Br_2 =$ 1 : 4 : 3 : 2 : 6) yield with sodium nitrite in acetic acid solution 6-*bromo-2-nitrothymol*, melting at 109—110°. The dibromothymol, prepared by the action of bromine in chloroform solution, is a viscid, colourless liquid boiling at 187—188° under 34 mm. pressure; the *acetyl* derivative melts at 54—55°. On attempting to brominate dibromothymol further, tetrabromo-*m*-cresol (m. p. 191—192°) is formed.

3 : 5-Dibromocarvacrol (3 : 5-dibromo-4-propyl-*o*-cresol)

($Me : Pr : OH : Br_2 = 1 : 4 : 2 : 3 : 5$)

is converted, when similarly treated, into 3 : 5-*dinitrocarvacrol*, which crystallises in needles melting at 116—117°.

s-Tribromoresorcinol [$(OH)_2 : Br_3 = 1 : 3 : 2 : 4 : 6$] is converted into 2 : 4-dibromo-6-nitroresorcinol, which crystallises in scales melting at 148—149°. It is noteworthy that the bromine atom replaced by the nitro-group is not one of the two atoms which are in the ortho-position relative to the same hydroxyl group. On reduction with tin and hydrochloric acid, 2 : 4-*dibromo*-6-*aminoresorcinol* is obtained as a very easily oxidisable hydrochloride; with acetic anhydride, a *tetra-acetyl* derivative is obtained as a yellow, crystalline powder melting at 123—125°. On treatment with nitric acid in acetic acid solution, 2-bromo-4 : 6-dinitroresorcinol is produced, two bromine atoms being eliminated, the one which occupies the position between the two hydroxyl groups remaining.

The effect of the presence of an aldehyde or carboxyl group was

investigated, using 3 : 5-dibromo-*p*-hydroxybenzaldehyde and 3 : 5-dibromosalicylic acid as examples. Nitrous acid attacks the hydroxyaldehyde but slowly, bromonitrohydroxybenzoic acid being probably produced. In the case of the salicylic acid, the reaction only begins at a high temperature, when the nitro-group replaces the carboxyl group, 2 : 4-dibromo-6-nitrophenol being formed. Nitric acid acts in a similar manner.

Although dibromodiphenol is attacked by nitric acid in acetone solution, no product could be isolated. Diphenylmethane derivatives, on the other hand, reacted easily with nitrous acid. In tetrabromodihydroxydiphenylmethane [$CH_2 : OH : Br_2 = 1 : 4 : 3 : 5$], a bromine atom is replaced in each nucleus, *dibromodinitrodihydroxydiphenylmethane* [$CH_2 : OH : Br : NO_2 = 1 : 4 : 3 : 5$] being formed and crystallising in golden-yellow needles melting at 232°; the *diacetyl* derivative melts at 185°. *Hexabromodihydroxydiphenylmethane*

$$[CH_2 : OH : Br_3 = 1 : 4 : 2 : 3 : 5]$$

yields *tetrabromodinitrodiphenylmethane* [either $CH_2 : OH : Br_2 : NO_2 = 1 : 4 : 2 : 3 : 5$ or $1 : 4 : 2 : 5 : 3$], which crystallises in dark yellow prisms melting at 244°; the *diacetyl* derivative melts at 167°.

When treated with nitrous acid, 2 : 4-dibromo-α-naphthol yields a blue compound and 4-bromo-2-nitro-α-naphthol. 1 : 6-Dibromo-β-naphthol behaves quite normally, yielding 6-bromo-1-nitro-β-naphthol, which Armstrong and Rossiter (Proc., 1891, 7, 87) obtained by the action of nitric acid on the dibromonaphthol. The *acetyl* derivative forms pale yellow needles melting at 115—117°. K. J. P. O.

Synthesis of Estragol and of Aromatic Derivatives containing an Unsaturated Chain. MARC TIFFENEAU (*Compt. rend.*, 1904, 139, 481—482. Compare Abstr., 1903, i, 241; Werner and Zilkens, Abstr., 1903, i, 615; Houben, Abstr., 1903, i, 805).—Phenylpropylene, CHPh:CHMe, is obtained by the action of β-bromostyrene on magnesium methyl iodide at a temperature of about 100°. Methylstilbene, CPhMe:CHPh, is similarly prepared from magnesium phenyl bromide and $MgBr{\cdot}O{\cdot}CPhMe{\cdot}CH_2Cl$ at 120—130°.

Allylbenzene, obtained by the action of allyl bromide on magnesium phenyl bromide in the cold, boils at 156—157°, has a sp. gr. 0·9012 at 15° and n_D 1·3143. Estragol synthesised from allyl bromide and the organomagnesium derivative of *p*-bromoanisole boils at 215—216°, has a sp. gr. 0·9755 at 15°, n_D 1·5236, and is converted by the action of alcoholic potash into anethole. M. A. W.

Naphthol-Yellow S. EDMUND KNECHT and EVA HIBBERT (*Ber.*, 1904, 37, 3475—3477. Compare Lauterbach, Abstr., 1882, 63).—Dinitro-α-naphtholsulphonic acid has been prepared and purified by Lauterbach's method; it crystallises in pale yellow needles containing $3H_2O$, and dissolves readily in water or alcohol. When anhydrous, it melts to a clear yellow liquid between 140° and 150°, which slowly decomposes below 175°. The potassium salt,

$$OK{\cdot}C_{10}H_4(NO_2)_2{\cdot}SO_3K,1\tfrac{1}{2}H_2O,$$

forms long, thin, elastic crystals of an orange-yellow colour. This salt, like all the others, turns red on warming and yellow again on

cooling, and explodes when strongly heated. The *sodium* salt contains $3H_2O$, the *ammonium* salt is anhydrous, and the *calcium* salt contains $4H_2O$. *Magnesium*, *silver*, *aniline*, and p-*nitraniline* salts have also been prepared. J. J. S.

Alkylamino-o dihydroxyacetophenones (Alkylaminoacetocatechols). Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 152814).—Chloroacetocatechol, $C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2Cl$, reacts with dimethylamine to form dimethylaminoacetocatechol, methylamine forming only a salt of the hydroxyketone (Dzierzgowski, Abstr., 1894, i, 234). When the chloro-compound is gently warmed with an excess of methylamine, however, *methylaminoacetocatechol*,

$$C_6H_3(OH)_2{\cdot}CO{\cdot}CH_2{\cdot}NHMe,$$

is produced, and is precipitated by ammonia from acid solutions as a white, crystalline powder, darkening at 200° and decomposing at about 230°. The *hydrochloride* crystallises from alcohol in colourless leaflets and decomposes at 240°. Ferric chloride gives an emerald-green coloration.

Ethylaminoacetocatechol, prepared in similar manner, forms microscopic crystals, the *hydrochloride* forms slender needles, and decomposes at 260°.

Ethanolaminoacetocatechol, from chloroacetocatechol and ethanolamine, is soluble in water, its *hydrochloride* crystallises from alcohol in leaflets, and melts at 197°. C. H. D.

Interaction of 1 : 3-Dicarbonyl Compounds and the Acetyl Derivatives of Dimethyl- and Phenyl-dihydroresorcinols. Walter Dieckmann and Richard Stein (*Ber.*, 1904, 37, 3370—3384. Compare Abstr., 1900, i, 482).—The action of acetic anhydride on 1 : 3-dicarbonyl compounds in presence of sodium acetate leads to the formation of the *C*-acetyl derivative; ethyl acetylmalonate, formed by this method, decomposes into ethyl acetoacetate, which is further acetylised. When acted on by acetic anhydride in absence of an alkaline acetate, dimethyl- and phenyl-dihydroresorcinols yield *O*-acetyl derivatives; ethyl acetoacetate and ethyl malonate do not react with acetic anhydride alone. Von Pechmann's formation of ethyl diacetoacetate by the action of acetic anhydride on ethyl acetoacetate (Abstr., 1894, i, 274) was probably due to the alkalinity of the glass boiling vessel, as the presence of traces of an alkali acetate are sufficient to bring about the reaction on prolonged boiling. This may be avoided by the addition of a small quantity of acetyl chloride.

The *O*-acetyl derivatives of 1 : 3-carbonyl compounds are converted into the corresponding *C*-derivatives when heated with anhydrous sodium acetate or with acetic anhydride and sodium acetate. When boiled with acetic anhydride and pyridine, quinoline, or dimethylaniline, ethyl acetoacetate yields the *O*-acetyl derivative; with acetic anhydride and concentrated sulphuric acid, it yields a mixture of the *O*- and the *C*-acetyl derivatives. With acetic anhydride and quinoline, dimethylaniline, or pyridine at the ordinary temperature, dimethyl- and phenyl-dihydroresorcinols yield the *O*-acetyl derivative, but the *C*-derivative when boiled with acetic anhydride and pyridine.

O-*Acetyldimethyldihydroresorcinol*, $\begin{array}{l}CMe_2\cdot CH_2\cdot C\cdot OAc \\ \vert \qquad\qquad\quad \Vert \\ CH{:}C(OH)\cdot CH\end{array}$, is a colourless, viscid oil, boils at 144° under 18 mm. pressure, has a neutral reaction, can be titrated with phenolphthalein as indicator, is hydrolysed slowly by water and rapidly by alkali hydroxides, with formation of acetic acid and dimethyldihydroresorcinol.

C-*Acetyldimethyldihydroresorcinol*, $\begin{array}{l}CMe_2\cdot CH_2\cdot C\cdot OH \\ \vert \qquad\qquad\quad \Vert \\ CH_2-CO-CAc\end{array}$, or

$$\begin{array}{l}CMe_2\cdot CH_2\cdot CO \\ \vert \qquad\qquad\; \vert \\ CH_2-CO-C{:}CMe\cdot OH\end{array},$$

crystallises in colourless needles, melts at 36°, boils at 127—128° under 14 mm., or at 250° under the ordinary pressure, and is soluble in all organic solvents, but only slightly so in water. It has a strongly acid reaction, is only partially precipitated from its solution in an aqueous alkali hydroxide on saturation with carbon dioxide, forms an ammonium salt as a momentary precipitate on addition of anhydrous ammonia to its ethereal solution, and is hydrolysed by boiling dilute sulphuric acid, but not by aqueous alkali hydroxides or baryta. With ferric chloride in alcoholic solution, it gives an intense yellowish-red coloration; the copper salt, $(C_{10}H_{13}O_3)_2Cu$, is blue, crystallises from alcohol, and melts at about 260°. The *anilide*, $C_{16}H_{19}O_2N$, crystallises in yellow needles and melts at 129—130°; the *phenylhydrazone* of the *phenylpyrazole* derivative, $\begin{array}{l}CH_2\cdot C(N\cdot NHPh)\cdot CH\cdot CMe \\ \vert \qquad\qquad\qquad\qquad\quad \Vert \\ CMe_2\cdot CH_2 \text{———} C-NPh\end{array}\!\!>\!N$, forms colourless needles, melts at 190°, dissolves in concentrated sulphuric acid to a blue solution, and gives Knorr's pyrazoline reaction after reduction with sodium and alcohol.

O-*Acetylphenyldihydroresorcinol* is a neutral, viscid oil, distils with partial decomposition at 200° under 14 mm. pressure, and is converted into the *C*-derivative when boiled with acetic anhydride and sodium acetate, pyridine, or tripropylamine.

C-*Acetylphenyldihydroresorcinol*, $\begin{array}{l}CHPh\cdot CH_2\cdot CO \\ \vert \qquad\qquad\quad \vert \\ CH_2-CO-CHAc\end{array}$, crystallises in long, colourless needles, melts at 104°, yields an unstable *bromine* derivative, and is oxidised by sodium hypobromite or hydrogen peroxide in aqueous sodium carbonate solution to β-phenylglutaric acid. The *alkali* salts are colourless, crystalline powders; the *copper* salt, $(C_{14}H_{13}O_3)_2Cu$, is a grey, insoluble, crystalline powder; the *anilide* forms colourless needles and melts at 124—125°; the *phenylhydrazone* of the *phenylpyrazole* derivative, $C_{26}H_{24}N_4$, crystallises in colourless needles, melts at 176—178°, dissolves in concentrated sulphuric acid to a dark green solution, and, after reduction with sodium and alcohol, gives a faint pyrazoline reaction.

Schwerin's acetyl-$\alpha\gamma$-diketohydrindene (Abstr., 1894, i, 194) closely resembles the *C*-acetyl derivatives of the dihydroresorcinol; it can be titrated with phenolphthalein as indicator, is not attacked by boiling aqueous alkali hydroxides, gives an intense yellowish-red coloration with ferric chloride, and forms a green *copper* salt, $(C_{11}H_7O_3)_2Cu$. It is a slightly stronger acid than the dihydroresorcinol compounds, and

is not, or only slightly, precipitated from its solution in aqueous alkali hydroxides on addition of carbon dioxide. G. Y.

Condensation of Aldehydes with *p*-Diketohexamethylene. Robert Stollé and W. Möring (*Ber.*, 1904, 37, 3486—3488).—Benzaldehyde condenses with *p*-diketohexamethylene in the presence of hydrogen chloride, forming *2-benzylquinol*, $C_6H_3(OH)_2\cdot CH_2Ph$, which crystallises from hot water in slightly coloured, glistening leaflets, melts at 105°, and boils at 230° under 13 mm. pressure. It dissolves readily in alcohol, ether, or alkalis, and reduces silver nitrate in the cold, or Fehling's solution on warming. Chromic acid oxidises it to *2-benzylquinone*, $C_6H_3O_2\cdot CH_2Ph$, crystallising in flat, yellowish-brown needles, melting at 43°, and dissolving readily in alcohol or ether.

2-Anisylquinol, $C_{14}H_{14}O_3$, prepared in similar manner from anisaldehyde and *p*-diketohexamethylene, melts at 126° and boils at 271° under 16 mm. pressure; the *dibenzoyl* derivative, $C_{28}H_{22}O_5$, forms a white powder and melts at 125°. *2-Anisylquinone*, $C_{14}H_{12}O_3$, forms glistening, orange leaflets and melts at 43°.

In the preparation of *p*-diketohexamethylene from ethyl succinosuccinate, a condensation product is obtained with the formula $C_{12}H_{14}O_3$, crystallising from alcohol in needles and melting at 133°.

C. H. D.

Picrates of Unsaturated Compounds. Giuseppe Bruni and E. Tornani (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 184—187).—The authors have experimented with the following pairs of compounds, the first members of which contain an allyl group ($\cdot CH_2\cdot CH:CH_2$) which is replaced in the isomerides by a propenyl group ($\cdot CH:CHMe$): methyleugenol and *iso*methyleugenol; safrole and *iso*safrole; ordinary apiole and *iso*apiole; apiole and *iso*apiole from dill oil; asarone; they find that those compounds containing allyl groups in the side-chain do not yield picrates, but that those with propenyl groups readily yield picrates, as may be seen by the red or reddish-brown coloration formed on mixing their solutions with solutions of picric acid. The formation of a picrate may hence be used as a test for the presence of an allyl or propenyl group in the side-chain of an aromatic compound.

iso*Methyleugenol picrate*, $C_{17}H_{17}O_9N_3$, crystallises from alcohol in reddish-brown needles which decompose rapidly and melt at 40—45°.

Asarone picrate, $C_{18}H_{19}O_{10}N_3$, forms very dark brown needles melting at 81—82°.

iso*Safrole picrate*, $C_{16}H_{13}O_9N_3$, crystallises from alcohol in stable, bright red needles melting at 73°.

Picrate of ordinary iso*apiole*, $C_{18}H_{17}O_{11}N_3$, separates from alcohol in minute, reddish-brown needles which melt at 89—90°.

Picrate of iso*apiole* from dill oil, $C_{18}H_{17}O_{11}N_3$, crystallises from alcohol in intensely red, prismatic needles which melt at 81°.

Cryoscopic measurements of the last two picrates in acetophenone show that they are completely resolved into their constituents.

T. H. P.

Isomeric Ethers of Pyrogallol. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1904, 25, 808—816. Compare Abstr., 1903, i, 89; this vol., i, 808).—Partial methylation of pyrogallol by means of a limited amount of potassium hydroxide and methyl iodide leads to the formation of a mixture of the methyl ethers which, on acetylation, yielded a mixture of the oily acetyl derivatives of the dimethyl ethers and the crystalline acetyl monomethyl ethers. Of the latter, that which is sparingly soluble in alcohol is 1 : 2-diacetoxy-3-methoxybenzene; the alcoholic mother liquors contain 1 : 3-*diacetoxy*-2-*methoxybenzene*, which forms monoclinic crystals, melts at 51—54°. 1 : 3-*Dihydroxy*-2-*methoxybenzene*, obtained by hydrolysis of the diacetyl derivative with dilute sulphuric acid, melts at 85—87° and boils at 154—155° under 24 mm. pressure. Hoffmann-La Roche's supposed 1 : 3-dihydroxy-2-methoxybenzene (*Chem. Centr.*, 1900, ii, 459) is probably 1 : 3-dihydroxy-4-methoxybenzene. G. Y.

Chemical Action of Light. FRANZ SACHS and SIEGFRIED HILPERT (*Ber.*, 1904, 37, 3425—3431. Compare this vol., i, 156).—When a solution of *o*-nitrobenzyl alcohol in benzene is exposed to the action of light, it rapidly becomes yellowish-green and deposits a yellow, flocculent precipitate, which becomes almost black on prolonged exposure to light. The *product*, $C_7H_5O_2N$, is amorphous, commences to decompose at 237°, and is easily soluble in alcohol, glacial acetic acid, or aqueous ammonia. On acidification of its ammoniacal solution, it separates as a rose-coloured to dark brown flocculent precipitate; on addition of ether to the alcoholic solution, it is obtained as a violet powder. It is distinguished from azobenzoic acid by its indifference to reducing reagents. When a solution of *o*-nitrobenzyl alcohol and phenylhydrazine in glacial acetic acid is exposed to light, evolution of nitrogen takes place, and a *product* is obtained which forms a brownish-yellow, crystalline powder, sinters at 160°, and, when heated quickly, melts at 184°.

The action of light on *o*-nitrobenzaldehyde dissolved in hydrogen cyanide, or on *o*-nitromandelonitrile, leads to the formation of *o*-nitrosobenzoic acid. G. Y.

Action of Organomagnesium Compounds on Alkylated Saccharins. FRANZ SACHS, F. VON WOLFF, and AL. LUDWIG (*Ber.*, 1904, 37, 3252—3268. Compare this vol., i, 266).—*Phenyldimethylcarbinol*-o-*sulphonethylamide*, $OH\cdot CMe_2\cdot C_6H_4\cdot SO_2\cdot NHEt$, prepared by the interaction of magnesium methyl bromide and "ethylsaccharin," crystallises in snow-white crystals melting at 109—110°; from ether, it crystallises in large, monoclinic crystals [$a : b : c = 0.9822 : 1 : 0.6324$; $\beta = 52°16'$]. When dissolved in concentrated sulphuric acid, the *sultam* crystallising in large, colourless plates melting at 40° is formed; heating with fuming hydrogen chloride converts it into a *benzylsulphone* of the constitution $C_6H_4{<}{\genfrac{}{}{0pt}{}{CMe_2}{SO_2}}{>}O$, melting at 106—107°.

Phenyldiethylcarbinol-o-*sulphonethylamide*, $OH\cdot CEt_2\cdot C_6H_4\cdot SO_2\cdot NHEt$, prepared from "ethylsaccharin" and magnesium ethyl bromide, crys-

tallises in large, colourless, monoclinic, holohedric crystals [$a:b:c = 0\cdot914:1:0\cdot577$; $\beta = 66°24'$]. C-*Diethyl*-N-*ethylbenzylsultam*,

$$C_6H_4{<}{}^{CEt_2}_{SO_2}{>}NEt,$$

obtained on dissolving in sulphuric acid and precipitating with water, melts at 140—150°. *Benzyldiethylsulphone*, $C_6H_4{<}{}^{CEt_2}_{SO_2}{>}O$, forms long, colourless, transparent, feather-like crystals melting at 91°.

*Phenyldi*iso*propylcarbinol*-o-*sulphonethylamide* crystallises in needles melting at 117—118°. *Phenyldi*iso*amylcarbinol*-o-*sulphonethylamide* forms large, flat prisms melting at 66—67°. *Triphenylcarbinol*-o-*sulphonethylamide* forms small, colourless prisms which melt at 184—185°. C-*Diphenyl*-N-*ethylbenzylsultam* melts at 155—165°, its *dinitro*-derivative melts between 220° and 230°, whilst the *diamino*-derivative, which forms yellow rhombohedra, becomes brown at 250°.

Phenyldimethylcarbinol-o-*sulphonmethylamide* melts at 105—106° and forms thin, monoclinic prisms as much as 4 cm. long [$a:b:c = 0\cdot9388:1:0\cdot5918$; $\beta = 56°5'$]. *Phenyldiethylcarbinol*-O-*sulphonmethylamide* melts at 111—112° and separates in rhombic, holohedric, transparent crystals [$a:b:c = 0\cdot9747:1:0\cdot5959$]. *Phenyldi*iso*propylcarbinol*-O-*sulphonmethylamide* crystallises in silvery tablets melting at 122—123°, the *di*iso*amyl* derivative melts at 81—82° and separates in stepped, four-sided prisms similar to common salt. *Triphenylcarbinol*-O-*sulphonmethylamide* forms hexagonal prisms melting at 194—195°; *diphenylbenzylsulphone* melts at 210°. The crystallography of many of these compounds is described in detail. E. F. A.

Colourless Salts of Triphenylcarbinol and Diphenylcarbinol. RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1904, **37**, 3058—3062).—The colourless *oxalate* of the carbinol base of malachite-green, $C_{23}H_{26}ON_2,2C_2H_2O_4,3H_2O$, prepared by mixing oxalic acid and the base at 0°, melts at 78° and on further heating is converted into the coloured oxalate, which has a metallic lustre, and melts at 110°. In a similar manner, tetramethyldiaminothiol forms a colourless *oxalate*,

$$3C_{23}H_{26}N_2S,2C_2H_2O_4,$$

which melts and decomposes at 140°; this, when kept, or when heated in aqueous solution, is converted into the coloured oxalate of malachite-green.

Tetramethyldiaminobenzhydrol forms a colourless zincochloride, $C_{21}H_{30}ON_2,ZnCl_2,2HCl$; the aqueous solution becomes blue on heating, but colourless again when the solution is cooled. E. F. A.

Action of Triphenylcarbinol on Hydroxylamine. ARTHUR MOTHWURF (*Ber.*, 1904, **37**, 3150—3152).—From the action of triphenylcarbinol on hydroxylamine, no definite product was obtained by Baeyer and Villiger (Abstr., 1902, i, 769), but the author finds that, if the use of methyl alcohol as the crystallising agent be avoided, *bistriphenylmethylhydroxylamine*, $C_{38}H_{31}ON$, is obtained; it separates from benzene in rhombic crystals and melts at 184°. It is also formed when an excess of the carbinol chloride acts on hydroxylamine; it has neither acid nor basic characters, does not reduce

Fehling's solution, and does not form acyl or nitroso-derivatives. It is easily decomposed when boiled with acids and is probably a $\beta\beta$-substituted hydroxylamine.

Triphenylmethylhydroxylamine, $C_{19}H_{17}ON$, prepared by the action of triphenylcarbinol chloride on an excess of hydroxylamine, separates from a mixture of benzene and light petroleum in tetragonal prisms with pyramidal ends and melts at 124—135°. It is a β-derivative, since it reduces cold Fehling's solution. It is a weak base and forms a *hydrochloride*, crystallising in needles; its *acetyl* derivative separates from light petroleum in hexagonal pyramids and melts at 98—102°. A. McK.

Hydroxyfuchsones. Franz Sachs and Richard Thonet (*Ber.*, 1904, 37, 3327—3334).—3 : 4-*Dihydroxytriphenylcarbinol*,

$$OH\cdot CPh_2\cdot C_6H_3(OH)_2,$$

prepared by the condensation of benzophenone chloride with catechol by means of concentrated sulphuric acid, forms a light yellow powder. When heated at 80—105°, it forms *quino-2-hydroxyfuchsone*, $CPh_2:C_6H_3O\cdot OH$, a dark orange-coloured powder, melting at 123° (compare Baeyer and Villiger, this vol., i, 786). The dyeing properties of the latter substance are interesting since it does not contain two hydroxyl groups in the ortho-position relatively to one another: its behaviour with mordants varies; with some it dyes marked colours, whilst with others there is little result.

Catecholdiphenylmethylene ether, $CPh_2{<}^{O}_{O}{>}C_6H_4$, prepared by gently heating catechol with benzophenone chloride without the presence of a condensing agent, separates from alcohol in colourless prisms and melts at 93°.

3 : 4-*Dihydroxy-3' : 4'-dimethoxytriphenylcarbinol*,

$$OH\cdot CPh[C_6H_3(OH)_2]\cdot C_6H_3(OMe)_2,$$

prepared by the action of benzoylveratrol chloride on catechol in the presence of aluminium chloride, melts at 73—74°; when heated at 80°, it is converted into its *fuchsone*.

When the chloride of Michler's ketone is condensed with catechol in the presence of sulphuric acid, Liebermann's proto-blue (tetramethyldiamino-3 : 4-dihydroxytriphenylcarbinol) is formed (compare Abstr., 1903, i, 861).

3 : 4-*Dimethoxytriphenylcarbinol*, $OH\cdot CPh_2\cdot C_6H_3(OMe)_2$, prepared by the action of magnesium phenyl bromide on benzoylveratrol, melts at 151·5°. When reduced by zinc and glacial acetic acid, it forms 3 : 4-*dimethoxytriphenylmethane*, $CHPh_2\cdot C_6H_3(OMe)_2$, melting at 110·5°.

3 : 4-*Dimethoxytriphenylchloromethane*, $CPh_2Cl\cdot C_6H_3(OMe)_2$, prepared by passing hydrogen chloride into a chloroform solution of dimethoxytriphenylcarbinol, melts at 148·5°. When slowly heated at 140°, it decomposes with formation of methyl chloride and a reddish-brown product, presumably the corresponding methoxyfuchsone. When dimethoxytriphenylcarbinol is heated with aniline and benzoic acid, the methoxy-groups are replaced by aniline groups, violet-red dyes being produced. A. McK.

Tri-*p*-tolylcarbinol. ARTHUR MOTHWURF (*Ber.*, 1904, 37, 3153—3163. Compare Gomberg, this vol., i, 489).—According to Baeyer and Villiger (Abstr., 1902, i, 769), the basicity of triphenylcarbinol is increased by the introduction of methoxyl groups; since the oxonium theory renders it probable that these basic characters are conditioned by the unsaturated nature of the oxygen atom, the author has studied tri-*p*-tolylcarbinol and finds that the introduction of the three methyl groups into triphenylcarbinol has much the same effect in increasing the basic character of the latter as has the introduction of a methoxyl group in the para-position.

Tri-*p*-tolylcarbinol (compare Gomberg, *loc. cit.*) was prepared from methyl *p*-toluate and magnesium *p*-tolyl iodide; when the oil, obtained after removal of the ether used as the solvent in this Grignard reaction, was dissolved in glacial acetic acid, *tri-*p*-tolylcarbinyl acetate*, separating in prisms and melting indefinitely at 87°, was obtained; by the action of dilute sodium hydroxide, it yields tri-*p*-tolylcarbinol, which melts at 96·5°, and with boiling glacial acetic acid forms a yellowish-green solution, and with concentrated sulphuric acid a greenish-red solution.

*Tri-*p*-tolylmethane*, prepared by the reduction of tri-*p*-tolylcarbinol with zinc dust and hydriodic acid, forms monoclinic prisms and melts at 53—54°. Tri-*p*-tolylcarbinyl chloride melts at 181°, whilst Gomberg gives 173°. *Tri-*p*-tolylchloromethane aluminium chloride*, $C_{22}H_{21}Cl,AlCl_3$, forms yellowish-green needles, which are instantly decomposed by water. *Tri-*p*-tolylcarbinyl bromide* forms yellow rhombohedra and melts at 161—163°. *Tri-*p*-tolylcarbinyl iodide* forms dark blue needles. Tri-*p*-tolylcarbinyl ethyl ether melts at 114°, whilst Gomberg gives 105°.

*Tri-*p*-tolylacetonitrile*, prepared by the action of mercuric cyanide on tri-*p*-tolylcarbinyl chloride, separates in rhombohedra and melts at 192°. *Tri-*p*-tolylcarbinyl thiocyanate* crystallises from ethyl acetate in needles and melts at 147—148°.

*Sodium tri-*p*-tolylmethanesulphonate*, prepared by adding a few drops of sulphuric acid and then sodium hydrogen sulphite to an alcoholic solution of tri-*p*-tolylcarbinol, forms silky needles and contains $1H_2O$.

*Tri-*p*-tolylcarbinylamine*, prepared by passing dry ammonia into a benzene solution of tri-*p*-tolylcarbinyl chloride, separates from a mixture of benzene and light petroleum in monoclinic prisms and melts at 97°; it is readily decomposed when boiled with water. Its *acetyl* derivative melts at 211°.

*Tri-*p*-tolylcarbinol anilide* (tri-*p*-tolylcarbinylaniline), prepared from tri-*p*-tolylcarbinyl chloride and aniline, separates from light petroleum in rhombic prisms and melts at 131°.

*Benzeneazotri-*p*-tolylmethane*, $Ph\cdot N_2\cdot C(C_6H_4Me_3)_3$, prepared by the action of phenylhydrazine on tri-*p*-tolylcarbinol, separates from methyl alcohol in yellow prisms and melts and decomposes at 113—116°. *Benzenehydrazotri-*p*-tolylmethane* is the initial product of the preceding action, but is rather unstable.

*β-Tri-*p*-tolylmethylhydroxylamine* forms monoclinic prisms and melts at 103—105°, is readily decomposed by acids, and reduces Fehling's solution. Its *acetyl* derivative melts at 157°. *Bistri-*p*-tolylmethylhydroxylamine* separates from light petroleum in needles and melts at 155°.

Although triphenylcarbinol does not yield crystalline nitro-derivatives (Baeyer and Villiger, Abstr., 1903, i, 811), tri-*p*-tolylcarbinol does. *Trinitrotri*-p-*tolylcarbinol*, prepared by nitrating with 68 per cent. nitric acid in the cold, crystallises from benzene in tetragonal prisms and melts at 162°. It does not form a chloride, nor does it combine with sodium hydrogen sulphite.

Hexanitrotri-p-*tolylcarbinol*, prepared by allowing tri-*p*-tolylcarbinol to remain in contact with fuming nitric acid for 12 hours, forms monoclinic prisms and melts at 253°. *Hexanitrotri*-p-*tolylmethane*, prepared from tri-*p*-tolylmethane in an analogous manner, forms monoclinic prisms and melts at 280°. A. McK.

Cholesterol. II. OTTO DIELS and EMIL ABDERHALDEN (*Ber.*, 1904, 37, 3092—3103. Compare Abstr., 1903, i, 819).—The acid formerly supposed to have the composition $C_{20}H_{32}O_3$ (*loc. cit.*) has in reality the formula $C_{27}H_{44}O_4$, and behaves on titration with potassium hydroxide as a dibasic acid; when titrated with sodium hydroxide, however, it appears to be a monobasic acid, owing to the formation of a very sparingly soluble mono-sodium salt. The *silver* salt formerly described has the formula $C_{27}H_{44}O_4Ag_2$, and the *ethyl* ester is an acid ester having the composition $C_{29}H_{48}O_4$. A double linking probably exists in the acid, but the behaviour of the latter with bromine or potassium permanganate is not conclusive. The *dimethyl* ester of the acid, prepared from the silver salt, crystallises from methyl alcohol in white prisms, sinters at 67°, and melts at 69°; the *monomethyl* ester, prepared by direct methylation, crystallises from acetone in thick, six-sided plates and melts at 125° (corr.).

Cholestenone, $C_{27}H_{44}O$, obtained by adding finely-powdered copper oxide to fused cholesterol, separates from methyl alcohol in well-formed, white crystals and melts at 78°; the *phenylhydrazone*, $C_{33}H_{50}N_2$, crystallises from ethyl acetate in yellow needles, sinters at 142°, and melts at 152°; the p-*nitrophenylhydrazone*, $C_{33}H_{49}O_2N_3$, crystallises from boiling acetone in orange-yellow prisms, softens at 160°, and melts indefinitely at about 195°. The *semicarbazone*,

$C_{28}H_{47}ON_3$,

separates from methyl alcohol in slender crystals, sinters at 222°, and melts at 240° (corr.). With hydroxylamine, cholestenone behaves as an $\alpha\beta$-unsaturated ketone. In warm weather, the two substances condense in methyl-alcoholic solution to form the *oxime*, $C_{27}H_{45}ON$, which crystallises from ethyl acetate and melts at 152° (corr.); in cooler weather, however, hydroxylamine becomes attached at the double linking to form the *additive*-compound, $C_{27}H_{47}O_2N$, which crystallises from acetone in small, four-sided plates and melts indefinitely between 142° and 147°. On warming the additive compound with dilute hydrochloric acid, the normal oxime is obtained.

Cholesteryl chloride is best prepared by mixing cholesterol with thionyl chloride. W. A. D.

Preparation of *cyclo*Citrylideneacetic Acid and its Derivatives. ALBERT VERLEY (D.R.-P. 153575).—Citrylideneacetic acid and its esters and nitrile are not converted into *cyclo*-derivatives by

the usual agents employed for the conversion of ψ-ionone into ionone. The conversion is, however, readily effected by means of syrupy phosphoric acid containing 6—8 per cent. of sulphuric acid at 35°. cyclo*Citrylideneacetic acid* forms a viscid syrup, becoming crystalline after several months.

Methyl citrylideneacetate, $C_{13}H_{20}O_2$, prepared from methyl hydrogen malonate, citral, and pyridine at 100° (compare Abstr., 1899, i, 768), boils at 133° under 16 mm. pressure. *Methyl* cyclo*citrylideneacetate*, a colourless liquid with odour of mignonette, boils at 138° under 17 mm. pressure; the *ethyl* ester boils at 141° under 17 mm. pressure and has an odour of violets. cyclo*Citrylideneacetonitrile* is a yellow liquid boiling at 141° under 17 mm. pressure; its odour resembles that of ionone. C. H. D.

Molecular Weights of the Yellow Nitroso-compounds. Frederick J. Alway and Ross A. Gortner (*Amer. Chem. J.*, 1904, 32, 400—403).—It has been shown by Alway and Bonner (Abstr., 1903, i, 764) that *p*-nitrosobenzaldehyde, which has a yellow colour, has a normal molecular weight in freezing and boiling benzene and in freezing acetic acid solutions.

The molecular weights of methyl and ethyl *p*-nitrosobenzoates, ethyl *m*-nitrosobenzoate, and methyl and ethyl *p*-nitrosocinnamates in solution in benzene have been determined by the cryoscopic method. The results obtained with the *p*-nitrosocinnamates are not conclusive, since the quantities employed were very small; the ethyl ester formed a greenish-yellow solution and produced a depression of the freezing point corresponding with 50 per cent. in the unimolecular and 50 per cent. in the bimolecular condition, whilst the methyl ester formed a yellow solution and gave a result corresponding with the bimolecular condition. The *p*-nitrosobenzoates showed the normal molecular weight.

Ethyl m-*nitrosobenzoate*, $NO \cdot C_6H_4 \cdot CO_2Et$, obtained by reducing ethyl *m*-nitrobenzoate with zinc dust and acetic acid and treating the product with ferric chloride, forms stellate groups of white crystals and melts at 52—53° to a green liquid. It exists in solution chiefly in the unimolecular condition, but at the temperature of freezing benzene a small proportion is present in the bimolecular condition.

E. G.

[*o*-Glycollylaminobenzoic Acid and the Synthesis of Indigo.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 153576 and 153577).—On fusing together anthranilic acid and glycollide at 180—200° for several hours, combination takes place,

$$C_6H_4{<}^{CO_2H}_{NH_2} + \begin{matrix} CO \\ | \\ CH_2 \end{matrix}{>}O = C_6H_4{<}^{CO_2H}_{NH \cdot CO \cdot CH_2 \cdot OH},$$

forming *o-glycollylaminobenzoic acid*, which melts at 167° and dissolves readily in hot water or organic solvents. Dilute acids or alkali hydroxides hydrolyse it on warming to glycollic and anthranilic acids.

o-Glycollylaminobenzoic acid is converted, on fusion with alkali hydroxide at 230—300°, into a mixture of indoxyl and an indoxylcarboxylic acid in proportions varying with the conditions of the

fusion. A satisfactory yield of indigo is obtained on oxidising the product. C. H. D.

Benzamidesulphonic Acid. A. Bühner (*Annalen*, 1904, 333, 283—288).—On attempting to prepare acetylbenzamide by the action of acetic anhydride on benzamide in the presence of sulphuric acid, an unstable compound, the *benzamide* salt of benzamidesulphonic acid, $NHBz\cdot SO_3H,NH_2Bz$, was formed. The free acid is unstable, but forms a series of stable salts and basic salts. It is decomposed into potassium phenyl sulphate by heating with potassium hydroxide, and by heating with aniline at 150—160° into benzanilide and ammonium phenylsulphamate, thus: $NHBz\cdot SO_3H,NH_2Ph + NH_2Ph = NHBzPh + NH_2\cdot SO_3H,NH_2Ph \longrightarrow NHPhSO_3\cdot NH_4$, two phases being recognised in the reaction.

The benzamide salt is prepared by adding benzamide to a cooled mixture of acetic anhydride and sulphuric acid; the temperature at first rises, and then the salt crystallises out; it melts at 145—146°. Its solution in ice-cold water is at first clear, but in a short time benzamide separates; if the latter is extracted with ethyl acetate and silver nitrate added to the solution, which has been carefully neutralised with sodium hydroxide, the *basic silver* salt of benzamidesulphonic acid, $C_7H_5O_4NSAg_2$, crystallises out in colourless leaflets. The normal *silver* salt, $C_7H_6O_4NSAg$, is prepared by warming a solution of the acid with silver oxide until it is neutral, adding acetone, filtering, and evaporating the filtrate to dryness under reduced pressure; it forms leaflets. Aniline benzamidesulphonate is prepared by adding aniline to an aqueous solution of the acid and evaporating to dryness; the salt melts at 120°. K. J. P. O.

Alkylation of Acid Amides. A. Bühner (*Annalen*, 1904, 333, 289—295).—When acid amides are treated with methyl sulphate at moderate temperatures, an additive compound is formed, which appears to be the salt of methyl hydrogen sulphate and an imino-ether; thus from benzamide is formed the salt $OMe\cdot CPh\vdots NH_2\cdot O\cdot SO_3Me$. In many cases the salt cannot be isolated in a pure state. It is suggested that this reaction is a case of 1 : 3-addition, in which the double linking between the carbon atom and the oxygen becomes a single linking, and the nitrogen becomes quinquevalent and doubly linked to the carbon.

Mol. proportions of benzamide and methyl sulphate are heated on the water-bath in benzene solution and the salt precipitated with alcohol; it crystallises in hygroscopic needles melting at 108—111°, and gives no precipitate with barium chloride; by alkali hydroxides, it is converted into benziminomethyl ether, boiling at 95—97° under 14—15 mm. pressure.

Methylbenzamide behaves in a similar manner, but the *additive* product is a viscid oil, from which the unstable methylated benziminomethyl ether can be obtained in a pure state.

The *additive* compound, $OMe\cdot CMe\vdots NHPh\cdot O\cdot SO_3Me$, prepared in a similar manner from acetanilide and methyl sulphate, is a very hygroscopic salt melting at 80—82°, and immediately decomposed into

methyl acetate and aniline methyl sulphate by water. The salt is converted into acetanilidomethyl ether by treatment with dry sodium carbonate in chloroform solution; the ether boils at 81—82° under 12 mm. pressure (compare Lander, Trans., 1901, 79, 691) and reacts with aniline giving diphenylethaneamidine (m. p. 131—132°).

Dimethylbenzamide and methylacetanilide yield oily additive products, whilst anthranil gives a very unstable, red, crystalline substance.

K. J. P. O.

Condensations with Amino-acids. V. Combination of Alanine and Glycine by means of Benzoylalanineazide. THEODOR CURTIUS and CHARLES FLORENT VAN DER LINDEN (*J. pr. Chem.*, 1904, [ii], 70, 137—157. Compare Curtius and Lambotte, this vol., i, 835).—*Benzoylalanylhydrazide*, $NHBz \cdot CHMe \cdot CO \cdot N_2H_3$, obtained by shaking ethyl benzoyl-α-aminopropionate with hydrazine hydrate in ethereal solution, crystallises in colourless needles and melts at 105—107°; the *hydrochloride* crystallises in slender needles; the *benzylidene* derivative, $NHBz \cdot CHMe \cdot CO \cdot NH \cdot N \colon CHPh$, forms needles and melts at 194°; the *β-propylidene* derivative, $C_{10}H_{11}O_2N_3 \colon CMe_2$, crystallises from water in needles which melt at 75—80°; after drying over sulphuric acid, it melts at 157·5°; the *benzoyl* derivative,

$$NHBz \cdot CHMe \cdot CO \cdot NH \cdot NHBz,$$

formed by the Schotten-Baumann reaction, crystallises in needles and melts at 180—184°. The action of sodium nitrite and acetic acid on the hydrazide leads to the formation of *benzoylalanylazoimide*,

$$NHBz \cdot CHMe \cdot CO \cdot N_3,$$

which forms a white, crystalline powder, melts at 54°, decomposes at 55°, detonates when heated on platinum, and dissolves in dilute sodium hydroxide to a momentarily bluish-yellow, fluorescent solution. When boiled with absolute methyl alcohol, the azoimide forms the *methylurethane*, $NHBz \cdot CHMe \cdot NH \cdot CO_2Me$, which crystallises in snowy needles and melts at 150°; the *ethylurethane*, formed by boiling the azide with ethyl alcohol, crystallises in white needles and melts at 140°. When boiled with aniline in ethereal solution, the azoimide forms the *anilide*, $NHBz \cdot CHMe \cdot CO \cdot NHPh$, which crystallises in white needles and melts at 163—165°; the p-*toluidide* forms glistening leaflets or needles and melts at 172—175°. Dibenzoylalanylhydrazide,

$$NHBz \cdot CHMe \cdot CO \cdot NH \cdot NH \cdot CO \cdot CHMe \cdot NHBz,$$

obtained in the aqueous filtrate from the azoimide, and by the action of iodine on benzoylalanylhydrazide in alcoholic solution, crystallises in colourless, slender needles and melts at 262°.

Benzoylalanylalanine, $NHBz \cdot CHMe \cdot CO \cdot NH \cdot CHMe \cdot CO_2H$, obtained by the action of benzoylalanylazoimide on alanine in concentrated aqueous and slightly alkaline solution, crystallises in colourless needles and melts at 170—171°; the *ethyl* ester is prepared by heating the silver salt with ethyl iodide, or, along with the ethyl ester of benzoylalanine, by shaking the acid with 1—3 per cent. alcoholic hydrogen chloride; both methods give a very small yield of the ester; it crystallises in colourless needles and melts at 148—149°.

Benzoylalanylalanylhydrazide,

$$NHBz \cdot CHMe \cdot CO \cdot NH \cdot CHMe \cdot CO \cdot N_2H_3,$$

crystallises in needles and melts at 183—184°; the *benzylidene* derivative is a colourless, flocculent, crystalline substance; it melts, with slight decomposition, at 230°. The *azoimide* was obtained in very small quantity; it detonates when heated on platinum.

Benzoylalanylaminoacetic acid, $NHBz\cdot CHMe\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, obtained by acting with benzoylalanylazoimide on glycine in slightly alkaline aqueous solution, crystallises in slender, colourless needles, melts at 166°, and gives no biuret reaction with Fehling's solution. The aqueous solution of the *ammonium* salt gives a granular, blue precipitate, $(C_{12}H_{13}O_4N_2)_2Cu$, with copper sulphate, a white precipitate, $C_{12}H_{13}O_4N_2Ag$, with silver nitrate, a reddish-brown precipitate with ferric chloride, and, after some hours, a white precipitate with barium chloride.

The *ethyl* ester crystallises in clusters of needles and melts at 108°; the *hydrazide* crystallises in slender, colourless needles and melts at 161—162°; the *benzylidene* derivative of the hydrazide forms colourless needles and melts at 226°; the *β-propylidene* derivative of the hydrazide crystallises in small, colourless needles and melts at 177°; the *azoimide*, which is a crystalline powder and melts and decomposes at 84°, is formed along with a substance which is probably dibenzoylalanylglycylhydrazide and melts at a high temperature.

Benzoylalanylglycylaminoacetic acid,

$$NHBz\cdot CHMe\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

formed from benzoylalanylglycylazoimide and glycine, or from benzoylalanylazoimide and glycylglycine hydrochloride, crystallises in colourless needles, melts and becomes brown at 204—205°, and gives the biuret reaction with Fehling's solution; the *silver* salt is a crystalline powder. G. Y.

Condensations with Amino-acids. VI. Formation of Compounds of Aspartic Acid by means of Hippurylazoimide. Theodor Curtius and Hans Curtius (*J. pr. Chem.*, 1904, [ii], 70, 158—194).—Hippurylazoimide condenses with aspartic acid in aqueous alkaline solution to *hippurylaminosuccinic acid*,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

which crystallises from hot water in strongly refractive, thick prisms and melts at 191°; the *silver* salt, $C_{13}H_{12}O_6N_2Ag_2,1\frac{1}{2}H_2O$, decomposes on exposure to light or when boiled with water; the *barium* salt, $C_{13}H_{12}O_6N_2Ba$, remains unchanged at 260°; the *dihydrazine* salt, $C_{13}H_{14}O_6N_2,2N_2H_4$, forms a white, flocculent precipitate and melts at 168—170°; the *copper* salt, $C_{13}H_{12}O_6N_2Cu,3H_2O$, is blue when freshly prepared, green when dried. The *diethyl* ester, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et$, is obtained either by the action of alcoholic hydrogen chloride on hippurylaminosuccinic acid or by the condensation of hippurylazoimide with diethyl aminosuccinate; it forms a white, crystalline powder and melts at 92°. The action of ethyl iodide on the silver salt leads to the formation of a viscid, red *syrup*, which in aqueous solution is colourless at the ordinary temperature, but at about 10° forms a blue jelly; if the solution is boiled until the evolution of iodine is complete, the colour reaction does not take place on cooling. The *dimethyl* ester is obtained

either by boiling the acid with methyl-alcoholic hydrochloric acid or by heating the silver salt with methyl iodide; it melts at 136°. If hydrazine hydrate is added to a boiling alcoholic solution of the dimethyl ether, the *dihydrazide*, $C_9H_8O_2N\cdot NH\cdot CH(CO\cdot N_2H_3)\cdot CH_2\cdot CO\cdot N_2H_3$, is formed; it separates from a concentrated aqueous solution in anhydrous crystals, from a dilute solution in crystals containing 1 mol. of water of crystallisation, and melts at 213·5°; the *hydrochloride*, $C_{13}H_{18}O_4N_6,2HCl$, decomposes at 125°; the *dibenzylidene* derivative melts at 204°; the *di-o-hydroxybenzylidene* derivative forms a voluminous, red precipitate and melts at 209°; the *di-β propylidene* derivative melts and decomposes at 183°; the *dibenzoyl* derivative,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH(CO\cdot N_2H_2Bz)\cdot CH_2\cdot CO\cdot N_2H_2Bz,$$

melts at 228°. The *diazoimide* is obtained by dissolving the dihydrazide in dilute hydrochloric acid and adding a concentrated solution of sodium nitrite to the well-cooled mixture; it melts at about 70°, decomposes suddenly when more highly heated, and dissolves in aqueous alkali hydroxides to a yellowish-red solution. When boiled with absolute alcohol until the evolution of nitrogen is completed, the diazoimide yields the *urethane*,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH(NH\cdot CO_2Et)\cdot CH_2\cdot NH\cdot CO_2Et,$$

which melts at 214° and on digestion with dilute sulphuric acid evolves carbon dioxide, and, with phenylhydrazine, yields glyoxalphenylosazone. When boiled with water, the diazoimide yields carbon dioxide, nitrogen, and a sparingly soluble precipitate. The *diamide*, formed by the action of ammonia on the diazoimide in ethereal or aqueous solution, crystallises in nacreous leaflets and melts and decomposes at 223°. The action of aniline on the diazoimide in ethereal solution leads to the formation of the *phenylcarbamide-anilide* derivative, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH(CO\cdot NHPh)\cdot CH_2\cdot NH\cdot CO\cdot NHPh$, which is obtained as a white powder and melts and decomposes at 218—220°. This product was heated with concentrated hydrochloric acid at 100° and the residue left on evaporation benzoylated by the Schotten-Baumann reaction; after extraction with light petroleum and water, the residue melted at 195° and was identical with Klebs' di-$\alpha\beta$-benzoylaminopropionic acid (Abstr., 1894, i, 439). The similar *derivative* obtained by the action of *p*-toluidine on the diazoimide melts at 216°.

Ethyl hippurylaspartylaminosuccinate,

$$\begin{array}{l}CO_2Et\cdot CH_2\cdot CH(CO_2Et)\cdot NH\cdot CO\cdot CH_2\cdot CH\cdot NH\cdot CO\cdot CH_2\cdot NHBz \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CO\cdot NH\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et\end{array},$$

obtained by acting with dry hippurylaspartyldiazoimide on ethyl aminosuccinate in ethereal solution. It forms a white powder, melts under 150°, gives the biuret reaction, and contains less than 1 mol. of hydrazoic acid, which is completely eliminated only on hydrolysis of the ester with an alkali hydroxide or baryta. The *acid*, $C_{21}H_{24}O_{12}N_4$, forms colourless, transparent, glistening crystals, becomes yellow at 80°, melts and decomposes at about 100°, and on prolonged boiling with aqueous baryta is partially hydrolysed to hippurylaspartic acid and aspartic acid. The *silver* salt, $C_{21}H_{20}O_{12}N_4Ag_4$, decomposes at about 172°; the *barium* salt, $C_{21}H_{20}O_{12}N_4Ba_2$, and the *lead* salt are described. The *tetrahydrazide*, $C_{21}H_{20}O_8N_4(N_2H_3)_4$, is a white powder, melts and

decomposes at 176°, and reduces ammoniacal silver solutions or Fehling's solution; the *tetrabenzylidene* derivative commences to sinter at 150°, and melts and decomposes, but not sharply, at a higher temperature; the *hydrazidediazoimide*,

$$\begin{array}{l} NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH\cdot CO\cdot NH\cdot CH(CO\cdot N_3)\cdot CH_2\cdot CO\cdot NH \\ \qquad\qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\quad CH\cdot CO\cdot NH\cdot CH(CO\cdot N_3)\cdot CH_2\cdot CO\cdot NH \end{array},$$

obtained by the action of hydrochloric acid and sodium nitrite on the tetrahydrazide, decomposes when heated on platinum, or when boiled with alcohol or water, and with aniline in ethereal solution yields a *hydrazidedianilide*, which decomposes at about 147°, and when heated with hydrochloric acid at 160° yields benzylideneazine on being shaken with benzaldehyde.

The hydrazidediazoimide and ethyl aminosuccinate form a white *product*, which evolves hydrazoic acid when hydrolysed by an alkali hydroxide and distilled with sulphuric acid. With hydrazine hydrate in alcoholic solution, the white product forms *hippuryldiaspartylaspartylpentahydrazide*,

$$\begin{array}{l} NH\cdot CO\cdot CH_2\cdot NHBz \\ | \\ CH\cdot CO\cdot NH\cdot CH[CO\cdot NH\cdot CH(CO\cdot N_2H_3)\cdot CH_2\cdot CO\cdot N_2H_3]\cdot CH_2\cdot CO\cdot NH \\ | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ CH\cdot CO\cdot NH\cdot CH[CO\cdot NH\cdot CH(CO\cdot N_2H_3)\cdot CH_2\cdot CO\cdot N_2H_3]\cdot CH_2\cdot CO\cdot NH \end{array},$$

which sinters at 151° and melts and decomposes at 175°; the *tetrabenzylidene* derivative sinters at 175° and melts and decomposes at about 190°.

Hippurylaspartyldiazoimide condenses with ethyl aminoacetate to *ethyl hippurylaspartyldiaminoacetate*, which melts at 195°. Hippurylazoimide and ethyl aminoacetate react in ethereal solution to form ethyl hippurylaminoacetate. G. Y.

Condensations with Amino-acids. VII. Formation of Derivatives of β-Amino-α-hydroxypropionic Acid and of β-Aminobutyric Acid by means of Hippurylazoimide. Theodor Curtius and Otto Gumlich (*J. pr. Chem.*, 1904, [ii], 70, 195—223).—The action of hippurylazoimide on β-amino-α-hydroxypropionic acid in aqueous alkaline solution leads to the formation of *α-hippuroxy-β-aminopropionic acid*, $NHBz\cdot CH_2\cdot CO\cdot O\cdot CH(CH_2\cdot NH_2)\cdot CO_2H$, which crystallises in stellate groups of white needles, melts at 176°, and gives the characteristic primary amine reactions; the *ammonium* and *silver* salts are described. The action of alcoholic hydrogen chloride leads to hydrolysis of the hippuroxy-group and formation of ethyl hippurate. Ethyl-α-hippuroxy-β-aminopropionate is formed by the action of ethyl iodide on the silver salt; it crystallises in slender needles and melts at 96°.

Hippuryl-β-aminobutyric acid,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2H,$$

obtained by treating β-aminobutyric acid with hippurylazoimide in alkaline solution, crystallises in sheaves of needles and melts at 122°; the *ammonium* salt forms white scales; the *silver* salt crystallises in sheaves of long needles; the *methyl* ester, obtained by boiling the acid with alcoholic hydrochloric acid, crystallises in colourless needles and melts at 104°; the *ethyl* ester crystallises in sheaves of needles and melts at 80°.

Hippuryl-β-aminobutyrylhydrazide crystallises in sheaves of long, colourless needles, melts at 188°, and reduces ammoniacal silver or Fehling's solution; the *hydrochloride* is hygroscopic and melts at 188°; the *benzylidene* derivative forms granular crystals and melts at 154°; the o-*hydroxybenzylidene* derivative crystallises in glistening leaflets and melts at 186°; the *β-propylidene* derivative forms a yellow, crystalline mass or white, glistening leaflets and melts at 145°. *Ethyl hippuryl-β-aminobutyrylhydrazidoacetoacetate*, obtained by shaking the hydrazide with ethyl acetoacetate, melts at 142°, and yields ethyl acetoacetate and the hydrazide when boiled with water. *s-Hippuryl-β-aminobutyrylhydrazide*, $(NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot CO)_2N_2H_2$, obtained by boiling the primary hydrazide with alcohol in presence of iodine, crystallises in white leaflets, begins to decompose at 255°, and melts at 264°. *Hippuryl-β-aminobutyrylazoimide* forms a finely-divided powder and decomposes suddenly at 73°. The *anilide*, obtained by acting with aniline on the azoimide in alcoholic solution, melts at 206°; the *amide* crystallises in white leaflets and melts at 173°. The *carbamide*, $(NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot NH)_2CO$, formed when the azoimide is boiled with water, crystallises in colourless needles and melts at 157°. The *methylurethane*,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot NH\cdot CO_2Me,$$

crystallises in colourless needles and melts at 151°; the *ethylurethane* crystallises in long needles and melts at 151°; when heated with concentrated hydrochloric acid at 110°, it is hydrolysed to benzoic acid, glycine, carbon dioxide, ethyl alcohol, and propylenediamine, which was characterised by conversion into its hydrochloride melting at 220° (Stache, Abstr., 1888, 1172). The *benzylurethane*, obtained from hippuryl-β-aminobutyrylazoimide and benzyl alcohol, crystallises in colourless needles and melts at 152—153°.

Hippuryl-β-aminobutyryl-β-aminobutyric acid,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2H,$$

obtained by treating β-aminobutyric acid with hippuryl-β-aminobutyrylazoimide in alkaline aqueous solution, crystallises in white leaflets and melts at 147°; the *ammonium* salt forms a white, crystalline mass; the *silver* salt crystallises in slender needles; the *ethyl* ester, obtained by boiling the acid with alcoholic hydrogen chloride, crystallises in white leaflets and melts at 103°; the *hydrazide* crystallises in white leaflets and melts at 194°; its hydrochloride forms a voluminous, flocculent, hygroscopic mass and melts at 194°. *Hippuryl-β-aminobutyryl-β-aminobutyrylazoimide* forms a finely-divided, yellow powder and decomposes suddenly at 78°. G. Y.

Condensations with Amino-acids. VIII. Hippuryl-γ-aminobutyric Acid and Hippuryl-β-phenyl-α-alanine. THEODOR CURTIUS and ERNST MÜLLER (*J. pr. Chem.*, 1904, [ii], 70, 223—229).—*Hippuryl-γ-aminobutyric acid*, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, formed by the action of hippurylazoimide on γ-aminobutyric acid, crystallises in delicate needles and melts at 176°; the *ammonium* salt forms colourless crystals and melts at 161—162°; the *silver* salt is obtained as a flocculent precipitate; the *ethyl* ester, formed by the alcoholic hydrogen chloride method, crystallises in colourless needles and melts

at 94°; the *hydrazide* crystallises in colourless, microscopic plates and melts and decomposes at 165—167°.

Hippuryl-β-phenylalanine, $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH(CH_2Ph)\cdot CO_2H$, obtained from β-phenylalanine (Erlenmeyer, Abstr., 1893, i, 581) and hippurylazoimide, crystallises in stellate groups of needles and melts at 172°; the *silver* salt is sensitive to light; the *ethyl* ester forms colourless needles and melts at 98°; the *hydrazide* crystallises in stellate groups of long needles, melts at 183°, and forms a *hydrochloride* which melts and decomposes at 186°; the *benzylidene* derivative melts at 158°; the *azoimide* decomposes at 70°. G. Y.

Condensations with Amino-acids. IX. The Action of Acylazoimides on Carbamide, and of Phenylcarbamic Azoimide on Glycine. THEODOR CURTIUS and WOLFGANG LENHARD (*J. pr. Chem.*, 1904, [ii], 70, 230—262. Compare Abstr., 1883, 337; 1896, i, 143, 647).—The action of hippurylazoimide on carbamide in various proportions leads to the formation of hippuric acid, but not of hippurylcarbamide; in one experiment, dibenzamidodihydroxytetrene (Rügheimer, Abstr., 1889, 249) was obtained. Benzoylcarbamide could not be obtained by acting with benzoyl chloride or benzoylazoimide on carbamide in slightly alkaline aqueous solution. Benzoylcarbamide and hydrazine hydrate do not enter into reaction in alcoholic solution, but on addition of benzoylcarbamide to hydrazine hydrate, an energetic reaction, resulting in the formation of benzoylhydrazide, takes place. Attempts to obtain condensation products by the action of phenylcarbamic azoimide (Abstr., 1899, i, 137) on carbamide and on biuret were without result. The action of phenylcarbamic azoimide on glycine in aqueous solution leads to the formation of phenylureidacetic acid (Paal, Abstr., 1894, i, 332); the *methyl* ester crystallises in colourless prisms and melts at 143°; the *hydrazide*,

$$NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot N_2H_3,$$

obtained by treating the methyl ester with hydrazine hydrate, crystallises in stellate groups of long needles and melts at 186·5°; the *hydrochloride*, $C_9H_{12}O_2N_4,HCl$, forms colourless, granular crystals and melts and decomposes at 191°; the *benzylidene* derivative crystallises in small, glistening leaflets and melts and decomposes at 227°; the *azoimide* crystallises in matted, delicate needles and melts and decomposes at 92°; the *amide*, $NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, crystallises in stellate clusters of needles and melts at 201°; the *anilide* forms small, colourless needles and melts at 214°; the *nitrosoanilide*, obtained by the action of nitrous acid on the anilide, is a yellow powder and melts and decomposes at 131°; the p-*toluidide* crystallises in colourless needles and melts at 229°; the *derivative* from *m*-tolylenediamine, $NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_6H_3Me\cdot NH_2$, forms matted, delicate needles and melts at 193°; the *phenylhydrazine* derivative, $NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot NHPh$, crystallises in long, glistening leaflets and melts at 227°. These amide and substituted amide derivatives are obtained by acting with the azoimide on the base. The *ethylurethane*, $NHPh\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO_2Et$, prepared by boiling the azoimide with alcohol, crystallises in microscopic, colourless needles, melts at 190°, and, when boiled with dilute sulphuric acid,

yields carbon dioxide, formaldehyde, ammonia, and aniline. The *benzylurethane* crystallises in microscopic needles and melts at 204°.

Ethyl phenylureidacetylaminoacetate,

$$NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

obtained by the condensation of phenylureidacetylazoimide with ethyl aminoacetate, crystallises in delicate, glistening leaflets, and melts at 165°. The *acid* is obtained by hydrolysing the ester with aqueous baryta or by adding phenylcarbamic azoimide to a solution of glycylglycine in aqueous sodium hydroxide; it crystallises in small, white needles and melts at 176°; [the *silver* salt crystallises in red needles and melts and decomposes at 202° The *hydrazide*,

$$NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot N_2H_3,$$

crystallises in small, colourless leaflets and melts and decomposes at 206°; the *hydrochloride* forms a snow-white powder and melts and decomposes at 200°; the *benzylidene* derivative is obtained as a sparingly soluble, flocculent precipitate; it melts and decomposes at 243°; the *β-propylidene* derivative forms a crystalline powder and melts and decomposes at 234°. The *azoimide* forms a brittle, transparent mass and, when freshly prepared, melts and decomposes at 108°; the *phenylhydrazide* crystallises in delicate, glistening leaflets and melts and decomposes at 139°; the *phenylcarbamide* derivative,

$$NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot NHPh,$$

formed by the action of aniline on the azoimide, melts and decomposes at 222°; the *methylurethane*,

$$NHPh\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NH\cdot CO_2Me,$$

melts and decomposes at 201°.

Ethyl phenylureidacetylglycylaminoacetate,

$$NHPh\cdot CO\cdot [NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2Et,$$

obtained by the condensation of phenylureidacetylaminoacetylazoimide with ethyl aminoacetate, crystallises in small, glistening leaflets and melts and decomposes at 203°. The *acid*, obtained by hydrolysis of the ester, crystallises in small leaflets, melts at 184°, and, when boiled with water, is decomposed with formation of phenylureidacetic acid. The *silver* salt is obtained as a white, very unstable precipitate. The *hydrazide* crystallises in small leaflets and melts and decomposes at 241°; the *hydrochloride* is a white powder which melts and decomposes at 215°; the *benzylidene* derivative is obtained as a white powder which melts at 247·5°. The *azoimide*, when quite freshly prepared, melts at 160—170°. The *ethylurethane* melts and decomposes at 244°, and yields formaldehyde and carbon dioxide when boiled with dilute sulphuric acid. G. Y.

m-Nitromethylenehippuric Acid. Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P. 153860).—In a similar manner to methylenehippuric acid (this vol., i, 413), m-*nitromethylenehippuric acid* may be prepared by the action of paraformaldehyde and sulphuric acid on *m*-nitrohippuric acid. The acid crystallises from alcohol as a yellowish-white powder, melts at 165°, and dissolves in hot alcohol, benzene, or chloroform, but is insoluble in water or ether.

C. H. D.

Synthesis of Polypeptides. IV. Derivatives of Phenylalanine. Emil Fischer (*Ber.*, 1904, 37, 3062—3071. Compare Abstr., 1903, i, 465, 607, 799, 800, and this vol., i, 652).—*a-Bromobenzylmalonic acid*, $CH_2Ph\cdot CBr(CO_2H)_2$, prepared by brominating benzylmalonic acid, melts, when dry, at 137° (corr.) and crystallises from water in twinned prisms and from chloroform in six-sided plates. On heating this for $\frac{1}{2}$—$\frac{3}{4}$ hour at 125—130°, *a-bromo-β-phenylpropionic acid*, $CH_2Ph\cdot CHBr\cdot CO_2H$, is obtained in the form of an almost colourless oil, which, when heated with ammonia, forms phenylalanine. This affords an excellent practical method for the synthesis of this amino-acid. *a-Bromo-β-phenylpropionylchloride* is a colourless oil of unpleasant odour, boiling at 132—133° (corr.) under 12 mm. pressure, which, when condensed with glycylglycine in sodium hydroxide solution, forms *a-bromo-β-phenylpropionylglycylglycine*; this melts at 157—158° (corr.), and is soluble in 8 parts of hot water, from which it crystallises in prisms. *Phenylalanylglycylglycine*,

$$CH_2Ph\cdot CH(NH_2)\cdot[CO\cdot NH\cdot CH_2]_2\cdot CO_2H,$$

crystallises in oblique plates melting and decomposing at 235° (corr.). *Cinnamoylglycylglycine*, $CHPh{:}CH\cdot[CO\cdot NH\cdot CH_2]_2\cdot CO_2H$, formed as a by-product when ammonia acts on a-bromo-β-phenylpropionylglycylglycine, melts at 229—235° (corr.) and crystallises in microscopic prisms. It can also be prepared by condensing cinnamoyl chloride with glycylglycine.

a-Bromo-β-phenylpropionyl-a-phenylalanine is formed to the extent of 35 per cent. of the theoretical quantity when phenylalanine is condensed with phenylbromopropionylchloride; it melts at 174—175° (corr.) and crystallises in colourless, octagonal plates. Ammonia converts it into *phenylalanylphenylalanine*,

$$CH_2Ph\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2Ph,$$

which crystallises from water, with $2H_2O$, in hexagonal prisms and melts and decomposes at 288° (corr.). As a by-product, *cinnamoylphenylalanine* is formed, which crystallises from alcohol in hexagonal plates melting at 198—199° (corr.), and is almost insoluble in water.

E. F. A.

Dinitriles and Amyl Nitrite. Jarl Lublin (*Ber.*, 1904, 37, 3467—3469. Compare Euler, this vol., i, 146, 230).—The compound obtained by E. von Meyer (Abstr., 1895, i, 582) by the action of nitrous acid on benzeneacetodinitrile [β-imino-β-phenylpropionitrile] is shown to be the *ammonium* derivative of a-iso*nitroso-β-nitrosoimino-β-phenylpropionitrile*, $NO\cdot N{:}CPh\cdot C(CN){:}N\cdot ONH_4$. It is obtained by the action of amyl nitrite on an ethereal solution of the dinitrile. Part of the dinitrile undergoes decomposition yielding ammonia and the compound $COPh\cdot C(CN){:}N\cdot OH$ (compare Meyer, *loc. cit.*). The ammonia and amyl nitrite then react with the remainder of the dinitrile yielding the ammonium salt.

β-Imino-β-*p*-tolylpropionitrile yields a similar *compound*,

$$C_6H_4Me\cdot C({:}N\cdot NO)\cdot C(CN){:}N\cdot ONH_4,$$

melting and decomposing at 156°, and the ethereal mother liquor yields the *compound* $C_6H_4Me\cdot CO\cdot C(CN){:}N\cdot OH$, melting at 130·5—131°.

β-Iminobutyronitrile yields the *compound*

$$NO \cdot N:CMe \cdot C(CN):N \cdot ONH_4,$$

melting at 122°. β-Imino-β-phenyl-α-methylpropionitrile yields no such ammonium salt with amyl nitrite in ethereal solution. J. J. S.

Nitrosocinnamic Acids and Esters. FREDERICK J. ALWAY and WALTER D. BONNER (*Amer. Chem. J.*, 1904, 32, 392—398).—p-*Nitrosocinnamic acid*, $NO \cdot C_6H_4 \cdot CH:CH \cdot CO_2H$, prepared by reducing *p*-nitrocinnamic acid with zinc dust and acetic acid and treating the product with ferric chloride at a temperature of 40—60°, forms a yellow, indistinctly crystalline powder which, on heating, does not melt but darkens above 220°; when freshly prepared, it is soluble in alcohol or glacial acetic acid, but if left for several days, it becomes partly insoluble in alcohol. The *ethyl* ester crystallises in yellow needles, melts at 72—73°, and is soluble in alcohol, benzene, or acetic acid. The *methyl* ester crystallises in lemon-yellow needles and melts at 111—112° (uncorr.); it is sometimes obtained in green crystals, which, on exposure to light, are gradually converted into the yellow modification.

Ethyl *m*-nitrocinnamate is slightly more volatile with steam than the corresponding *p*-compound. m-*Nitrosocinnamic acid* crystallises in stellate groups of small, white needles, which gradually turn brown on exposure to moist air; on heating, it decomposes without melting at 230°. The *ethyl* ester crystallises in green, rhombic plates, melts at 65—66° (uncorr.), and is readily soluble in alcohol. E. G.

Transformation of β-Aminoamides into β-Ketoamides. ICILIO GUARESCHI (*Atti R. Accad.*, *Torino*, 1903—1904, 39, 823—828).—The aminobenzylacetamide (β-aminocinnamide) previously prepared by the author (Abstr., 1897, i, 168) crystallises in shining, colourless laminæ, exceedingly soluble in acetic acid and less so in water, alcohol, or ether. In solution, it has a neutral reaction and its aqueous or alcoholic solution is coloured violet-red by ferric chloride. Neither ferrous sulphate nor copper acetate precipitates it. It melts at 164·5—165°, and at higher temperatures sublimes, giving ammonia and a carbonaceous residue. When dissolved or suspended in water and treated with potassium nitrite solution and a trace of sulphuric acid, or when exposed in the solid state to the nitrous vapours from a mixture of potassium nitrite and sulphuric acid, it assumes a red colour. On heating with water, it takes up water and loses ammonia, yielding benzoylacetamide, which melts at 114—116°; Obregia gave the melting point 111—113° for this compound (Abstr., 1892, 324).

Methylaminobenzylacetomethylamide (*β-methylaminocinnamomethylamide*), $NHMe \cdot CPh:CH \cdot CO \cdot NHMe$, obtained together with benzoylacetomethylamide by the interaction of methylamine and ethyl benzoylacetate, crystallises from ether in shining prisms and from alcohol in needles melting at 118—119°. It dissolves in water, but on boiling or evaporating the aqueous solution, an odour of methylamine is emitted. When exposed in the dry state to the action of nitrous vapours, it assumes a red colour, whilst with ferric chloride it

gives an intense violet coloration. On boiling with water, it yields benzoylacetomethylamide and methylamine:

$$NHMe\cdot CPh\colon CH\cdot CO\cdot NHMe + H_2O = CH_2Bz\cdot CO\cdot NHMe + NH_2Me.$$

Benzoylacetomethylamide, obtained as just described, crystallises in shining, heavy plates melting at 104—105°. In the solid state, it is not coloured by nitrous vapours, but ferric chloride produces an intense violet coloration. T. H. P.

*iso*Cinnamic Acid. EMIL ERLENMEYER, jun. (*Ber.*, 1904, 37, 3361).—Recent publications by Michael (Abstr., 1903, i, 418, 698) and by Liebermann (Abstr., 1903, i, 255, 485) appear to cast doubt on the existence of *iso*cinnamic acid, discovered by Erlenmeyer, sen.

The author confirms his father's experiments. *iso*Cinnamic acid melting at 37° was isolated and the crystallographic measurements agreed with those formerly made by Haushofer.

*iso*Cinnamic acid readily undergoes change; thus, the clear crystals, when separated from their solution, become turbid, whilst the melting point also changes. A. McK.

Thorium Salts of Certain Organic Acids. GILBERT T. MORGAN (*Pharm. J.*, 1904, [iv], 19, 472).—*Thorium salicylate, cinnamate*, and the three *coumarates* have been prepared by the interaction of the soluble alkali salts of the organic acids with thorium nitrate in aqueous solution. The *oleate*, prepared by mixing equivalent quantities of hydrated thorium oxide and oleic acid, has the consistence of lard. Thorium compounds have also been obtained with phenol, 2:4:6-tribromophenol, *p*-cresol, resorcinol, pyrogallol, α- and β-naphthols, gallic acid, and tannic acid. The *phthalate* and *camphorate* are sparingly soluble in water, whilst the other derivatives are insoluble. All these compounds are amorphous substances to which no very definite formula can be assigned.

Thorium *lactate*, $(OH\cdot CHMe\cdot CO_2)_4Th,2H_2O$, forms opaque, white, tabular, deliquescent crystals. The *benzenesulphonate*, $(C_6H_5\cdot SO_3)_4Th$, forms small, colourless crystals. The *naphthalene-α-sulphonate*, $(C_{10}H_7\cdot SO_3)_4Th$, and the corresponding *naphthalene-β-sulphonate* are soluble in water. The *phenol-*p*-sulphonate* (sulphocarbolate),

$$(OH\cdot C_6H_4\cdot SO_3)_4Th,9H_2O,$$

crystallises in pale pink, transparent prisms and is much more radioactive than the insoluble oleate obtained by precipitation (compare Rutherford and Soddy, Trans., 1902, 81, 321, 837). The *β-naphthol-6-sulphonate*, $(OH\cdot C_{10}H_6\cdot SO_3)_4Th,9H_2O$, forms colourless crystals. The *camphorsulphonate*, $(C_{10}H_{15}O\cdot SO_3)_4Th,9H_2O$, crystallises from water in colourless, transparent, lustrous prisms. E. G.

Mechanism of the Transformation of βγ-Unsaturated α-Hydroxy-acids into the Isomeric γ-Ketonic Acids. EMIL ERLENMEYER, jun. (*Ber.*, 1904, 37, 3124—3128. Compare Abstr., 1903, i, 676).—Largely a theoretical paper. It is shown that the first product of the transformation of phenyl-α-hydroxycrotonic acid under the influence of acetic anhydride containing a few drops of sulphuric

acid is Δ^{β}-phenylcrotonolactone, and this fact is considered to prove that the first step in the transformation of $\beta\gamma$-unsaturated α-hydroxy-acids is the wandering of the α-hydroxyl group according to the scheme: $CHPh{:}CR{\cdot}CH(OH){\cdot}CO_2H \longrightarrow OH{\cdot}CHPh{\cdot}CR{:}CH{\cdot}CO_2H$.

W. A. D.

α-Phenyl-*o*-hydroxycinnamonitrile and α-Phenylcoumarin. WALTHER BORSCHE and F. STREITBERGER (*Ber.*, 1904, 37, 3163—3167).—Salicylaldehyde and benzyl cyanide condense in the presence of sodium hydroxide to form *α-phenyl-o-hydroxycinnamonitrile*,

$$OH{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}CN,$$

which separates from aqueous methyl alcohol in yellow needles and melts at 104°. When boiled with dilute hydrochloric acid, it is converted into 3-phenylcoumarin, $C_6H_4<\begin{matrix}CH{:}CPh\\ O\text{—}\overset{|}{C}O\end{matrix}$, which separates in needles and melts at 140°. By the action of concentrated sodium ethoxide solution, 3-phenylcoumarin is converted into α-phenylcoumarinic acid, which did not undergo transformation into the isomeric α-phenylcoumaric acid. α-Phenyl-*o*-hydroxycinnamonitrile could not be converted into 2-hydroxy-3-phenylquinoline.

A. McK.

Derivatives of α- and β-Naphthisatins. CAMILLE DREYFUS and HENRY DREYFUS (D.R.-P. 153418. Compare this vol., i, 832).—The method employed for the preparation of naphthalides of naphthisatin may also be employed to prepare the corresponding anilides and toluidides. The hydrocyanocarbodiarylimides are prepared from the corresponding thiocarbamides, and probably have the constitution $R^{II}{:}CR^{I}{\cdot}CN$, where R^{I} is the residue of α- or β-naphthylamine, and R^{II} is the residue of β-naphthylamine, aniline, *o*-toluidine, or *p*-toluidine.

Hydrocyanocarbo-β-naphthylphenylimide melts at 146°; *hydrocyanocarbo-β-naphthyl-*o*-tolylimide* at 106°; *hydrocyanocarbo-β-naphthyl-*p*-tolylimide* at 129°; *hydrocyanocarbo-β-naphthyl-α-naphthylimide* at 165°; *hydrocyanocarbo-α-naphthylphenylimide* at 121°; *hydrocyanocarbo-α-naphthyl-*o*-tolylimide* at 97°, and *hydrocyanocarbo-α-naphthyl-*p*-tolylimide* at 151°.

Warm sulphuric acid converts these compounds into the corresponding isatin derivatives, acid amides being formed as intermediate products. Alkali sulphides reduce the isatin derivatives to naphthaleneindigotin compounds.

C. H. D.

Preparation of Indoxylic Acid and Indoxyl. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 152548).—In the preparation of indoxylic acid and indoxyl from salts of phenylglycine-*o*-carboxylic acid, the salt is intimately mixed with the alkali hydroxide in the dry state. If mixed in aqueous solution and evaporated before fusion, the yield is reduced to 25—30 per cent. A yield of 90 per cent. is, however, obtained if the evaporation is performed in a vacuum, the temperature being gradually raised to 180—200°, when the reaction sets in.

C. H. D.

Bromination of Indigotin. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 151866. Compare this vol., i, 57, 167, 587).—In the bromination of indigotin in the presence of water, bromoisatin is produced (this vol., i, 500). This is avoided when the indigotin is made into a paste with 78 per cent. sulphuric acid, that is, of such strength that indigotin sulphate, but no sulphonated derivative, is formed, and bromine is then added. The proportion of bromine in the products, which resemble those obtained by dry bromination, may be varied. C. H. D.

Optically Active *p*-Methoxymandelic Acids. EDUARD KNORR (*Ber.*, 1904, 37, 3172—3176).—Ostwald has shown that the electrical conductivity of anisic acid is only slightly less than that of benzoic acid, whilst Baeyer and Villiger (Abstr., 1902, i, 770) observed that the basic character of triphenylcarbinol is enormously increased by the introduction of methoxyl groupings. The author has accordingly investigated the effect on the optical activity of mandelic acid by the methoxylation of this acid in the *p*-position.

Anisaldehyde cyanohydrin crystallises in prisms and melts at 66—67°. When its imino-ether hydrochloride, prepared by the action of dry hydrogen chloride on a mixture of the cyanohydrin and ethyl alcohol, is hydrolysed, *ethyl* p-*methoxymandelate*,

$$OMe\cdot C_6H_4\cdot CH(OH)\cdot CO_2Et,$$

is formed; this separates from water or from light petroleum in needles and melts at 47—48°.

p-*Methoxymandelamide*, obtained as a by-product, separates from ethyl alcohol in silky leaflets and melts at 163—164°. r-p-*Methoxymandelic acid*, obtained by hydrolysis either of the ethyl ester or of the amide, crystallises in leaflets and melts at 108—109°. When the crop obtained by neutralising it with cinchonine is repeatedly crystallised from water, cinchonine *d*-*p*-methoxymandelate is obtained. The separation of *r*-*p*-methoxymandelic acid into its optically active components is conveniently attained on the larger scale by aid of a nucleus of the cinchonine *d*-salt, according to the method used by Lewkowitsch, Rimbach, and McKenzie for the preparation of *d*-mandelic acid.

One hundred c.c. of water dissolve, at 10°, 0·506 gram of the cinchonine *d*-salt (m. p. 160°) and 0·637 gram of the cinchonine *l*-salt (m. p. about 174—175°), d- and l-p-*Methoxymandelic acids* separate from water in monoclinic, sphenoidal crystals melting at 104—105° and contain $2H_2O$. The crystals were measured. The *d*-acid gives $[\alpha]_D + 146·14°$ at 19° (sp. gr. = 1·0047), and the *l*-acid $[\alpha]_D^{\circ} - 145·24°$ at 16° (sp. gr. = 1·0053), the solvent being water in each case. The introduction of the methoxyl grouping in the *p*-position into mandelic acid accordingly lowers the specific rotation of the latter by about 10°.

The inactive *p*-methoxymandelic acid is racemic, and not a *dl*-mixture, since its crystalline form is different from that of the active isomerides. A. McK.

The Two Isomeric Hydrocinnamylidenemalonic Acids. C. N. RIIBER (*Ber.*, 1904, 37, 3120—3124).—Thiele and Meisenheimer's $\alpha\delta$-hydrocinnamylidenemalonic acid,

$$CH_2Ph\cdot CH\dot{:}CH\cdot CH(CO_2H)_2$$

(Abstr., 1899, i, 603), is shown to have the structure attributed to it; the oxidation of its methyl ester giving phenylacetic acid, malonic acid, and carbon dioxide. *Methyl αδ-hydrocinnamylidenemalonate*, $CH_2Ph{\cdot}CH{:}CH{\cdot}CH(COMe)_2$, boils at 123° under 0·16 mm. and at 187° under 12 mm. pressure, undergoing in the latter case considerable decomposition.

αδ-Hydrocinnamylidenemalonic acid, when kept in a closed tube, gradually changes into the *γδ-isomeride*, $CH_2Ph{\cdot}CH_2{\cdot}CH{:}C(CO_2H)_2$; in presence of concentrated hydrochloric acid, the change is complete in about a month. The product crystallises from benzene in small bundles of needles and melts at 124°; its structure follows from its giving hydrocinnamic and oxalic acids on oxidation with alkaline potassium permanganate. W. A. D.

Phthalyl Derivatives of α-Aminopropionic Acid. Rudolf Andreasch (*Monatsh.*, 1904, 25, 774—784).—*Ethyl phthalyl-α-aminopropionate*, $C_6H_4{:}(CO)_2{:}N{\cdot}CHMe{\cdot}CO_2Et$, formed by the action of potassium phthalimide on ethyl α-bromopropionate at 140°, crystallises from carbon disulphide in large plates, from alcohol in thick needles, and melts at 65°. When heated with dilute sulphuric acid at 120°, the ester is hydrolysed to phthalic acid, alanine, and ethyl alcohol; the action of chlorosulphonic acid leads to the same hydrolysis, but with decomposition of the alanine.

Phthalylalanine, $C_6H_4{:}(CO)_2{:}N{\cdot}CHMe{\cdot}CO_2H$, is formed by heating phthalic anhydride with alanine at 160—170°. It crystallises in sheaves of needles, melts at 164°, and is soluble in boiling water, alcohol, acetone, or ether. The *phenyl* ester, obtained when phthalylalanine is heated with phenol and phosphorus oxychloride, crystallises in small needles and melts at 99°.

Phthaloylalanine, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,H_2O$, is obtained by boiling ethyl phthalyl-α-aminopropionate with baryta in aqueous solution or by warming phthalylalanine with aqueous potassium hydroxide. The acid crystallises from warm water, melts at 129°, is soluble in alcohol, ether, or glacial acetic acid, is hydrolysed to phthalic acid and alanine on prolonged warming with water, and yields phthalylalanine when dried at high temperatures. The action of potassium phthalimide on ethyl αβ-dibromopropionate leads to the formation of an oil, $C_5H_7O_2Br$, which has a suffocating odour and is probably a condensation product of ethyl bromoacrylate. G. Y.

Benzylphthalimide and Benzyl*iso*phthalimide. F. M. Jaeger (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 77—82).—The paper contains crystallographic measurements of these two compounds and of a second form of benzylphthalimide obtained on one occasion from benzene solution. This form is designated as the β-compound, and passes before fusion into the more stable α-compound, melting at 115·5°.

α-Benzylphthalimide is triclino-pinacoidal [$a:b:c = 0·8443:1:1·3600$; $\alpha = 108°24'$; $\beta = 120°7'$; $\gamma = 73°8'$]; β-benzylphthalimide, monoclino-prismatic, [$a:b:c = 0·8476:1:0·5092$; $\beta = 70°42'$]; benzylphthal*iso*imide, monoclino-prismatic [$a:b:c = 1·2303:1:0·5932$; $\beta = 71°46'$]. Attention

is drawn to the similarity of the ratio $a:b$ with the two forms of the first compound and to the similarity of the ratio $b:c$ with the β-modification and the isomeric *iso*imide. The author has observed similar relationships in the ratio $a:b$ with the red α- and the less stable yellow β-forms of 3 : 4-dinitrodiethylaniline.

The α- and β-benzylphthalimides are probably desmotropically related. G. D. L.

Action of Persulphates on Aromatic Nitriles. PAUL KATTWINKEL and RICHARD WOLFFENSTEIN (*Ber.*, 1904, 37, 3221—3227. Compare Abstr., 1901, i, 594).—*Terephthalicmonothiamide*,

$$CO_2H\cdot C_6H_4\cdot CS\cdot NH_2,$$

formed by the action of hydrogen sulphide on cyanobenzoic acid, melts at 247°; *terephthalhydroxamide*, $NH_2\cdot C(N\cdot OH)\cdot C_6H_4\cdot CO_2H$, is not melted at 320°.

Terephthalamic acid is not melted on heating to 300°, but sublimes about 250°; it forms a colourless, amorphous *silver* salt, a *methyl* ester melting at 201°, and is converted on boiling with alkali into terephthalic acid. o-*Toluamide* crystallises in glistening needles melting at 147°, m-*toluamide* in rhombic prisms which melt at 97°. When acted on with potassium persulphate, *p*-toluonitrile yields *p*-cyanobenzoic acid, *p*-dibenzyldinitrile, and an amorphous, brown powder with a molecular weight of about 1200; whilst when oxidised with permanganate or chromic acid respectively, terephthalamic acid and *p*-toluic acid are the chief products. E. F. A.

The Condensing Influence of Potassium Persulphate on the Toluic Acids. CARL FISCHER and RICHARD WOLFFENSTEIN (*Ber.*, 1904, 37, 3215—3220).—*Dibenzyl*-4 : 4′-*dicarboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot CO_2H,$$

formed by the action of potassium persulphate on *p*-toluic acid, is a colourless, amorphous substance which is not melted at 320°; the *methyl* ester melts at 119°, the *ethyl* ester separates from alcohol in bright yellow needles melting at 100°, the *chloride* forms plates and cubes melting at 119°. Dibenzyl-2 : 2′-dicarboxylic acid, prepared in the same way from *o*-toluic acid, melts at 231° and is identical with the acid described by Graebe (*Ber.*, 1875, 8, 1055) and Dobreff (*Annalen*, 1887, 239, 67). E. F. A.

Action of Eosin Solution on Oxidisable Substances. WALTHER STRAUB (*Chem. Centr.*, 1904, ii, 655; from *Arch. exp. Path. Pharm.*, 51, 383—390).—Iodine is liberated from a solution of potassium iodide in the presence of eosin and oxygen in the light. This reaction also occurs in the dark, but very slowly. In strong solutions of the iodide, the amount of iodine set free is proportional to the amount of eosin and the length of time. In very dilute solutions, the same amount of eosin liberates the more iodine in the same time, the more the eosin is diluted. This is explained by the fact that in dilute solutions the active rays, which give a green fluorescence, can penetrate the whole fluid, whilst in concentrated solutions they are absorbed at the surface. For the complete discharge of colour from eosin, 65

molecules of oxygen are required per molecule of eosin. The reaction probably depends on the formation of eosin peroxide. W. D. H.

Substances contained in "Orchil" Lichens. RONCERAY (*Bull. Soc. chim.*, 1904, [iii], 31, 1097—1103. Compare Juillard, this vol., i, 593).—Erythrin (erythric acid) was isolated from *Roccella Montagnei* (compare Hesse, Abstr., 1898, 531, 679) and *Dendrographa leucophæa*; lecanoric acid was obtained from *Roccella tinctoria*; whilst orcinol was found in all three lichens. Lecanoric acid was isolated by extracting the plant with warm alcohol (95°), converting the crude acid into the calcium salt, and crystallising the regenerated acid from alcohol. It melted at 201° on the Maquenne block. Erythrin was obtained by extracting the plants with dilute acetic acid (20 per cent.) and crystallising from alcohol by addition of chloroform; it melted at 164° on the Maquenne block (compare Juillard and Hesse, *loc. cit.*). T. A. H.

Gattermann's Reaction for the Synthesis of Aromatic Aldehydes. Application to *p*-Xylene. CURIO M. MUNDICI (*Gazzetta*, 1904, 34, ii, 114—124).—Francesconi and the author (Abstr., 1903, i, 426) have shown that when *p*-xylene is used in Gattermann's reaction for the synthesis of aromatic aldehydes, intermolecular change occurs, 2 : 4-dimethylbenzaldehyde being formed.

In order to confirm this result, which is at variance with the work of Harding and Cohen (Abstr., 1901, i, 725), the author has prepared dimethylcinnamic acids: (1) from 2 : 5-dimethylbenzaldehyde prepared by Bouveault's method (Abstr., 1896, i, 649, and 1897, i, 530); (2) from *m*-xylene, and (3) from *p*-xylene, both by Gattermann's synthesis. The dimethylcinnamic acids obtained by the last two methods are identical, and different from that yielded by the first method.

Hence, in the action of the hypothetical formyl chloride in the nascent condition on *p*-xylene, one methyl group is displaced from the para- to the meta-position with regard to the other, whilst the aldehyde group assumes the place left vacant by the displacement of the methyl.

That this displacement is due to the influence of the aluminium chloride employed is shown by the fact that when this condensing agent is allowed to act under conditions similar to those prevailing in Gattermann's synthesis, on *p*-xylene, part of the latter is transformed into *m*-xylene. T. H. P.

A Third Modification of Aldoximes. ERNST BECKMANN (*Ber.*, 1904, 37, 3042—3044).—*anti*Anisaldoxime exists both as platelets melting at 45° and needles melting at 64°; these can be mutually converted into one another. *anti*Benzaldoxime, when crystallised from water, melts at 16°; a modification melting at 5° is obtained on rubbing the strongly cooled, melted aldoxime. Cuminaldoxime, when crystallised from light petroleum, melts at 61°; when crystallised from water, it melts at 48°, whilst a third crystalline form melts at 35°. The author, for the moment, regards these modifications as monotropic. E. F. A.

Halogen-nitro- and Nitroamino-benzophenones. FRANZ KUNCKELL [and L. SZULC] (*Ber.*, 1904, 37, 3484—3486. Compare Consonno, this vol., i, 676).—3 : 3′-*Dibromodinitrobenzophenone*, $C_{13}H_6O_5N_2Br_2$, prepared by heating *m*-dibromobenzophenone with fuming nitric acid, separates from benzene in pale yellow crystals and melts at 209°. Alcoholic ammonia converts it at 130° into 3-*bromo*-3′-*aminodinitrobenzophenone*, $C_{13}H_8O_5N_3Br$, crystallising from alcohol in yellow, glistening leaflets and melting at 250°. Piperidine reacts with 3 : 3′-dibromodinitrobenzophenone at 125°, forming 3 : 3′-*dipiperidinodinitrobenzophenone*, $C_{23}H_{26}O_5N_4$, which crystallises from alcohol in yellow needles or from acetic acid in leaflets and melts at 190°.

4 : 3′-*Dibromobenzophenone*, $C_{13}H_8OBr_2$, prepared by heating *p*-bromobenzophenone with bromine and water at 160°, melts at 130° and reacts with fuming nitric acid to form 4 : 3′-*dibromodinitrobenzophenone*, $C_{13}H_6O_5N_2Br_2$, separating from benzene and acetic acid in yellow crystals and melting at 181°. Alcoholic ammonia converts it at 130° into 3′-*bromo*-4-*aminodinitrobenzophenone*, $C_{13}H_8O_5N_3Br$, crystallising from alcohol in small, yellow needles and melting at 240°. The same compound is obtained from 4-chloro-3′-bromodinitrobenzophenone.

3′-*Bromo*-4-*piperidinodinitrobenzophenone*, $C_{18}H_{16}O_5N_3Br$, crystallises from alcohol in yellowish-red needles, melts and decomposes at 76°, and dissolves in alcohol or chloroform. C. H. D.

Dibenzylideneacetone and Triphenylmethane. ADOLF BAEYER and VICTOR VILLIGER [and, in part, HENRY BASSETT, jun.] (*Ber.*, 1904, 37, 3191—3215. Compare Abstr., 1902, i, 380, 769 ; 1903, i, 811 ; 1904, i, 308).—o-*Aminotriphenylcarbinol*, prepared by the interaction of methyl anthranilate and magnesium phenyl bromide, crystallises in colourless plates from ether and melts at 121·5°. Only colourless salts have been obtained, although the momentary existence of coloured salts is indicated by the very fugitive blue colour of the hydrochloride of the carbinyl chloride when brought into contact with water. The *hydrochloride* crystallises in colourless, prismatic needles, which on heating become brown at 140° and melt and decompose at 164° ; the *hydrochloride* of the *carbinyl chloride*, $C_{19}H_{17}NCl_2$, crystallises in short, transparent, rectangular prisms. The *picrate* separates from benzene in bright, yellow, rhombic plates, melting and decomposing at 122·5—123·5°, whilst the dichloride, on heating with pyridine, forms *anhydro*-o-*aminotriphenylcarbinol*, $(C_{19}H_{15}N)_2$, which crystallises in colourless prisms, sparingly soluble in neutral solvents and melting and decomposing at 250° ; its *acetate* crystallises in large prisms melting at 134·5—137° and is converted by dilute acids into *acetyl*-o-*aminotriphenylcarbinol*, which melts at 192°.

o-*Aminotriphenylmethane*, obtained by reducing the carbinol with zinc dust and acetic acid, crystallises from ether in plates melting at 128—130° or from benzene in octahedra, which contain a molecule of the solvent and melt at 94—95° ; the *acetyl* derivative forms thick, colourless prisms melting at 154—155° ; the *benzoyl* compound melts at 94—95°, the *hydrochloride* crystallises in many-faced prisms, the *sulphate* in needles, the *oxalate* in platelets, and the *nitrate* in very slender needles.

Methyl phenylanthranilate, an odourless, viscid, colourless oil, boiling at 216·5—217·5° under 18·5 mm. pressure, interacts with magnesium phenyl bromide to form o-*phenylaminotriphenylcarbinol*, which crystallises in colourless prisms melting at 127·5—128·5° and forms an *anhydride*, 5 : 5-*diphenylhydroacridine*, $C_{25}H_{19}N$, melting at 243·5—244·5°, and forming an *acetate* melting at 216·5—218·5.

o-*Dimethylaminotriphenylcarbinol* crystallises from light petroleum or alcohol in short, colourless, flat prisms melting at 156—160°. The *dichloride*, which has only been obtained as a syrup, shows a well-marked, but fugitive, blue-violet coloration when brought into contact with water, the *hydrochloride* forms large prisms containing a molecule of water, melting at 149—157° or when anhydrous at 187°; the *picrate*, which crystallises in sparingly soluble yellow rhombs, being specially characteristic.

o-*Methylaminotriphenylmethane*, formed by the action of hydrogen chloride on dimethylaminotriphenylcarbinol, crystallises from benzene in rhombohedra melting at 130—132° and forms an *acetate* melting at 147·5—148·5°; the *hydrochloride* forms prisms, which soften at 190° and melt and decompose at 210°, the *sulphate* crystallises in needles, the *oxalate* in rhombic plates, and the *nitrate* in aggregates of needles.

The reactions of *o*-aminotriphenylcarbinol resemble those of the para-compound as regards the formation of a salt and also those of a bimolecular carbinol anhydride. E. F. A.

Additive Compounds of Dibenzylideneacetone and Hydrogen Chloride. Fritz Straus (*Ber.*, 1904, 37, 3277—3293. Compare Baeyer, Abstr., 1902, i, 380, 769; Vorländer, 1903, i, 496; Thiele and Straus, *ibid.*, i, 707).—Dibenzylideneacetone, in dry ethereal solution, is capable of forming definite compounds with certain metallic salts. With mercuric chloride, the *compound* $C_{17}H_{14}O,HgCl_2,OEt_2,HgCl_2$ is obtained. It crystallises in dark yellow, strongly refractive prisms, begins to sinter at 115—120°, and rapidly decomposes at 185°. The ether is firmly united; even when left for several days in a vacuum the crystals remain clear. Sodium chloride solution or chloroform decomposes them. When left in contact with dry hydrogen chloride, it forms the orange-coloured *compound*,

$$C_{17}H_{14}O,HgCl_2,OEt_2,HgCl_2,HCl,$$

which melts at 129°. A *compound*, $C_{17}H_{14}O,HCl,HgCl_2$, is formed when a dry ethereal solution of hydrogen chloride is added to an ethereal solution of the ketone and mercuric chloride. It separates in the form of voluminous, orange-coloured crystals which gradually become transformed into compact needles. It sinters at 125—128° and melts sharply at 134° to a dark liquid and is not decomposed by chloroform or benzene.

The *compound* $C_{17}H_{14}O,FeCl_3$ crystallises in brown needles with a brilliant green lustre, melts at 163°, and is decomposed by alcohol, but not by hot chloroform. Dry hydrogen chloride converts it into the *compound* $C_{17}H_{14}O,HCl,FeCl_3$, which has a carmine-red colour. The same compound combined with ether,

$$C_{17}H_{14}O,HCl,FeCl_3,OEt_2,$$

is obtained when a solution of hydrogen chloride and ferric chloride in dry ether is added to the red benzylideneacetone dihydrochloride.

A *compound* $(C_{17}H_{14}O)_2,H_2PtCl_6,OEt_2$ has been obtained by a similar method; it crystallises in carmine-red, glistening prisms. A second *compound* with $2Et_2O$ has also been obtained. Dibenzylideneacetone in ethereal solution reacts with fuming hydrochloric acid yielding a compound $C_{17}H_{14}O,HCl$, which crystallises in yellow needles. On exposure to the air, it rapidly decomposes into its components, and on mixing with an ethereal solution of hydrogen chloride or with the dry gas it yields the red dihydrochloride.

A solution of chloroplatinic acid transforms the yellow hydrochloride into the compound $(C_{17}H_{14}O)_2,H_2PtCl_6,2H_2O$, which crystallises in brick-red needles; ferric chloride yields the red compound,

$$(C_{17}H_{14}O)_2HCl,FeCl_3,H_2O.$$

When an ethereal solution of the colourless hydrochloride (Abstr., 1903, i, 707) is shaken with water, the aqueous solution gives a neutral reaction, but on the addition of nitric acid and silver nitrate gives a minute amount of precipitate. The addition of an ethereal solution of hydrogen chloride to a colourless solution of this hydrochloride in ether produces an intense yellow coloration and the product formed yields, on addition of bromine in chloroform solution, a certain amount of dibenzylideneacetonetetrabromide. There is thus probably equilibrium between the systems: colourless hydrochloride $\rightleftarrows$ ketone and hydrogen chloride $\rightleftarrows$ yellow labile hydrochloride (decomposed by water). The addition of ethereal solutions of ferric chloride or mercuric chloride to ethereal solutions of the colourless hydrochloride produces crystalline precipitates of the compounds described above, for instance, $C_{17}H_{14}O,HCl,HgCl_2$.

J. J. S.

Addition of Acids to $\alpha\beta$-Unsaturated Ketones. DANIEL VORLÄNDER and CARL SIEBERT (*Ber.*, 1904, **37**, 3364—3370. Compare Abstr., 1903, i, 495, 496; this vol., i, 65, 450, 535, 659).—Two pairs of additive isomeric hydrobromides of dibenzylideneacetone are known, two isomeric monohydrobromides, A and B, and two isomeric dihydrobromides, 2A and 2B.

Dibenzylideneacetone dihydrobromide, 2B, prepared by passing dry hydrogen bromide over dibenzylacetone for 16—20 hours, separates from a mixture of light petroleum and amyl alcohol in tetragonal plates. At the ordinary temperature, it gradually becomes brown, and sometimes hydrogen bromide is evolved from it. By the action of sodium ethoxide, it is converted into *dibenzylideneacetone hydrobromide*, B, which separates from a mixture of light petroleum and amyl alcohol in glistening leaflets, which become yellow at 75°, orange at 90°, and melt at 119—121° to a reddish-brown liquid. On being kept in a desiccator it gradually becomes brown, but is more stable than the dihydrobromide. Dry hydrogen bromide very readily converts it into the di-compound.

When hydrogen bromide is passed into a benzene solution of the hydrobromides B or 2B at 0°, a mixture of dibenzylideneacetone and the hydrobromide B is produced.

By the action of bromine on the hydrobromides B and 2B, either the tetrabromide melting above 200° or *tribromodibenzylacetone* having the probable composition $CHPhBr\cdot CH_2\cdot CO\cdot CHBr\cdot CHPhBr$ is formed, according to the amount of bromine used. The latter separates from alcohol in white needles, which become yellow at about 125° and melt at 134—137°; it may also be obtained by passing dry hydrogen bromide into a solution of the dibromide,

$$CHPh\colon CH\cdot CO\cdot CHBr\cdot CHPhBr,$$

in glacial acetic acid.

Dibenzylideneacetone is coloured orange by bromine vapour, whilst its hydrobromide A becomes red. Bromine vapour causes dianisylideneacetone to become reddish-violet, anisylideneacetophenone brown, anisylidenebenzylideneacetone violet-red to brown, dibenzylidene*cyclo*pentanone reddish-orange, and difurfurylidene*cyclo*pentanone black. These colorations are not caused by hydrogen haloids.

A. McK.

Benzopinacone and Benzopinacolin. Amand Valeur (*Compt. rend.*, 1904, 139, 480—481).—The product of the reaction of methyl or ethyl oxalate on magnesium phenyl bromide is benzopinacone (compare Abstr., 1903, i, 416), and not β-benzopinacolin, as stated by Dilthey and Last (compare this vol., i, 667). M. A. W.

Alkyloxyanthranoles. Carl Liebermann, A. Glawe, and Simon Lindenbaum (*Ber.*, 1904, 37, 3337—3343).—The study of alkyloxyanthranoles begun by Liebermann has been extended.

Alkyloxyanthranoles were formerly converted into their chlorides by means of phosphorus pentachloride; the chlorides are easily prepared by passing hydrogen chloride into chloroform or benzene solutions of alkyloxyanthranoles. *Phenylanthrone chloride*,

$$CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CPhCl,$$

crystallises in needles and melts at 168—169°. *Phenylanthrone bromide* forms needles melting at 145—147°. *Phenylanthrone*-p-*toluidide*, $C_{14}H_8OPh\cdot NH\cdot C_7H_7$, prepared from phenylanthrone chloride and *p*-toluidine, forms yellow needles and melts and decomposes at 174—178°.

Alkylanthrone chlorides act on metals. When benzene solutions of ethyl-, *iso*butyl-, and *iso*amyl-anthrone chlorides respectively are left in contact with zinc turnings in an atmosphere of carbon dioxide, they gradually assume a yellow colour, which disappears in the presence of air.

When a benzene solution of phenylanthrone chloride is shaken with mercury for several days, a current of dry oxygen being passed through the liquid during this time, a product free from chlorine is obtained; this melts at 219° and is probably the peroxide, $(C_{20}H_{13}O_2)_2$. When a benzene or chloroform solution of phenyloxanthranole is treated with hydrogen iodide, crystals of *phenylanthranole periodide hydriodide*, $(C_{20}H_{14}O,HI)_2I_3$, are obtained; this forms a brown solution with glacial acetic acid or acetone, and the addition of water causes the separation of phenylanthranole.

Other iodine compounds of the anthraquinone series are described. When hydrogen iodide is passed into a benzene solution of anthraquinone, dark crystals, like those of iodine, separate. *Anthranole diiodide*, $C_{14}H_{10}OI_2$, prepared by mixing concentrated benzene solutions of anthranole and iodine, forms dark leaflets. Chrysazin forms dark crystals with hydriodic acid. Quinazarin, anthrarufin, and alizarin also form compounds with hydriodic acid. A. McK.

Chloro-1 : 7-dihydroxyanthraquinone. R. Wedekind & Co. (D.R.-P. 153194. Compare this vol., i, 813).—1 : 7-Dihydroxyanthraquinone resembles the β-hydroxyanthraquinones in being able to take up chlorine in alkaline solution. Not more than one atom of chlorine can be introduced in this way, although two atoms are taken up by the β-hydroxyanthraquinones. The chlorine atom enters a β-position. *Chloro*-1 : 7-*dihydroxyanthraquinone* dissolves very readily in hot alcohol or acetic acid, readily in ether, sparingly in benzene. It melts and decomposes on heating, hydrogen chloride being evolved.

C. H. D.

[Sulphonic Acids of *p*-Diaminoanthrarufin Dialkyl Ether.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 152013).—Alkali sulphites convert the dinitro-derivatives of dihydroxyanthraquinone alkyl ethers, especially the alkyl ethers of *p*-dinitroanthrarufin, into ethers of diaminosulphonic acids. The alkyl ethers of *p*-diaminoanthrarufinsulphonic acid are violet dyes, and are readily hydrolysed, yielding *p*-diaminoanthrarufinsulphonic acid. C. H. D.

"Exodin." F. Zernik (*Chem. Centr.*, 1904, ii, 709; from *Apoth.-Zeit.*, 19, 598—600).—"Exodin" (this vol., i, 809) is not the tetramethyl ether of diacetylrufigallic acid, but a mixture of the hexamethyl ether of rufigallic acid, the pentamethyl ether of acetylrufigallic acid, and the tetramethyl ether of diacetylrufigallic acid. The physiological action is due to the presence of the first-named compound, the other two components being inactive. The hexamethyl ether of rufigallic acid, $C_{20}H_{20}O_8$, prepared from the residue after extracting commercial "exodin" tablets with chloroform, evaporating, crystallising from benzene, and hydrolysing with alcoholic potash, crystallises from ethyl acetate in pale yellow needles and melts at 245°; it is not attacked by an aqueous or a cold alcoholic solution of potassium hydroxide, and does not give Bornträger's aloin reaction, but forms a purple-violet coloration with concentrated sulphuric acid. The tetramethyl ether, $C_{18}H_{16}O_8$, and the pentamethyl ether of rufigallic acid may be isolated from the mother liquor of the hexamethyl ether. The former crystallises from ethyl acetate or chloroform in yellow, prismatic leaflets and melts at 235—237°; it dissolves in a large quantity of aqueous potassium hydroxide solution, forming a blood-red solution, and with concentrated sulphuric acid it gives a purple-violet coloration. The pentamethyl ether, $C_{19}H_{18}O_8$, crystallises from ethyl acetate or boiling alcohol in yellow needles and melts at 192—194°; it dissolves in concentrated sulphuric acid forming a purple-red solution, and with aqueous potassium hydroxide solution gives a dark-red coloration without appreciably dissolving. This compound was found to be

identical with Klobukowski's tetramethyl ether of rufigallic acid (Abstr., 1877, ii, 618). The *methyl ether* of diacetylrufigallic acid, $C_{22}H_{20}O_{10}$, crystallises from ethyl acetate in yellow leaflets and melts and decomposes at 262°; it is very sparingly soluble in alcohol or ether, more soluble in benzene, ethyl acetate, or glacial acetic acid, and very readily so in chloroform. It is not attacked by a cold aqueous solution of potassium hydroxide, but dissolves in concentrated sulphuric acid forming a purple violet solution. The *pentamethyl ether* of acetylrufigallic acid, $C_{21}H_{20}O_9$, forms yellow leaflets, which begin to melt about 179—180° but become completely liquid only about 209°. This compound is somewhat more readily soluble in ethyl acetate than the preceding substance, but resembles it in other properties. The tetramethyl and pentamethyl ethers of rufigallic acid with their acetyl derivatives give Bornträger's aloin reaction. E. W. W.

Condensation of Cochenillic Acid with Succinic Acid. CARL LIEBERMANN and HUGO VOSWINCKEL (*Ber.*, 1904, 37, 3344—3348).—*Cochenillic anhydride* is obtained by boiling a mixture of cochenillic acid, acetyl chloride, and phosphorus oxychloride, when the *acetic acid* derivative is formed; this separates from glacial acetic acid in prisms and forms the anhydride when heated at 115°. When cochenillic anhydride is fused with a mixture of succinic acid and succinic anhydride at 200—205°, *dihydroxydimethylethinediphthalide*, $CO<\genfrac{}{}{0pt}{}{C_6H_2Me(OH)}{O}>C{:}CH{\cdot}CH{:}C<\genfrac{}{}{0pt}{}{C_6H_2Me(OH)}{O}>CO$, is produced as a yellow, crystalline mass, which may be heated to 330° without its melting; it forms a yellow solution with concentrated sulphuric acid. When cochenillic anhydride is fused with succinic anhydride at about 160°, dihydroxydimethylethinediphthalidedicarboxylic acid is formed in small amount.

*Dihydroxydimethyl*iso*ethinediphthalide* (*tetrahydroxydimethylnaphthacenequinone*), $OH{\cdot}C<\genfrac{}{}{0pt}{}{CH{:}CMe{\cdot}C{\cdot}C(OH){:}C{\cdot}CO{\cdot}C \text{——} CH}{CH \text{——} C{\cdot}C(OH){:}C{\cdot}CO{\cdot}C{\cdot}CMe{:}CH}>C{\cdot}OH$, prepared by heating dihydroxydimethylethinediphthalide with sodium methoxide at 140—145°, crystallises in red needles, which may be heated to 330° without melting; its alcoholic solution exhibits orange fluorescence. Sodium chloride precipitates it from its alkaline solution, which is cochineal-red in colour. A. McK.

Menthones. CAMILLE MARTINE (*Ann. Chim. Phys.*, 1904, [viii], 3, 49—144).—In addition to a full account of work already published (compare Abstr., 1901, i, 559; 1902, i, 629; 1903, i, 315), this paper contains the following corrections and additions: the benzylidenementhone, melting at 51°, crystallises in the monoclinic system [$a : b : c = 1{\cdot}3285 : 1 : 1{\cdot}2749$; $\beta = 95°34'$]; the compounds described as oximes of the benzylidenementhones are hydroxylamine derivatives, $CH_2<\genfrac{}{}{0pt}{}{CH_2{\cdot}CHMe}{CHPr^{\beta}\text{—}CO}>CH{\cdot}CHPh{\cdot}NH{\cdot}OH$, yielding, on reduction, hydroaminobenzylidenementhol,

$$CH_2<\genfrac{}{}{0pt}{}{CH_2 \text{——} CHMe}{CHPr^{\beta}{\cdot}CH(OH)}>CH{\cdot}CHPh{\cdot}NH_2,$$

boiling at 205—208° under 15 mm. pressure; by using Haller's method for the preparation of sodiomenthol (compare this vol., i, 600), a slightly better yield of benzylidenementhone is obtained than by the original method, and the following derivatives were similarly prepared: methylmenthone, obtained by the action of methyl iodide on sodiomenthone, is a colourless liquid with an odour like that of camphor, boils at 96—97° under 13 mm. pressure, has a sp. gr. 0·9173 at 18°/18° and $[\alpha]_D$ +44°15′, and gives a *semicarbazone* melting at 203—204°; ethylmenthone, similarly prepared, boils at 106—108° under 15 mm. pressure, has a sp. gr. 0·9208 at 18°/18° and $[\alpha]_D$ +82°32′; *anisylidenementhone*, prepared by the action of anisaldehyde on sodiomenthone, forms colourless crystals melting at 115—116°, has $[\alpha]_D$ −278°26′, and forms a *hydroxylamine* derivative melting at 165—166°; *piperonylidenementhone* has not been isolated, but the *hydroxylamine* derivative forms colourless needles melting at 173—174°. M. A. W.

Action of Salicylic Acid on Terebenthene. E. Tardy (*J. Pharm. Chim.*, 1904, 20, [vi], 57—58).—When salicylic acid is boiled with terebenthene, a bornyl salicylate is formed, which melts at 44—45° and has $[\alpha]_D$ −34°20′. The compound displays triboluminescence, and is soluble in alcohol and ether, but insoluble in water.

G. D. L.

Preparation of Solid Camphene. Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P. 153924. Compare this vol., i, 680).—Solid camphene, free from chlorine, is readily obtained by the action of alkali hydroxides or ammonia on pinene hydrochloride dissolved in solutions of alkali soaps. When pinene hydrochloride is heated with dry powdered soap, the product is also free from chlorine, but a large excess of alkali soap is required. In solution, only ½ mol. of soap is necessary. C. H. D.

Constituents of the Ethereal Oil of "Amorpha Fruticosa." Vittorio Pavesi (*Chem. Centr.*, 1904, ii, 224; from *Rend. R. Ist. Lomb. sci. lett.*, [ii], 37, 487—494).—The portion of the oil boiling below 250° contains a terpene boiling between 150° and 220°, having n_D 1·4811 at 15·5° and a sp. gr. 0·8717 at 15°. The portion boiling at 250—270° contains cadinene and another sesquiterpene which has n_D 1·50652 at 15° and a sp. gr. 0·916 at 15°; it forms a liquid hydrochloride and resembles clovene. It is possibly a new sesquiterpene, $C_{15}H_{24}$ for which the name *amorphene* is suggested. N. H. J. M.

Composition of Patchouli Oil. Hugo von Soden and Wilhelm Rojahn (*Ber.*, 1904, 37, 3353—3355. Compare this vol., i, 604).—Patchouli oil was fractionated: two fractions of sp. gr. 0·984 and 1·002 at 15° respectively, consisting mainly of patchouli alcohol, whilst other two fractions of sp. gr. 0·946 and 0·964 respectively at 15° were submitted to further fractionation and yielded a fraction A with the sp. gr. 0·930—0·940 at 15° and α_D about −50°, and a fraction B with the sp. gr. 0·930—0·940°. After fraction A had been hydrolysed, it yielded a

sesquiterpene, $C_{15}H_{24}$, boiling at 264—265° under 750 mm. pressure and having the sp. gr. 0·9335 at 15° and α_D −58°45′ at 20°. After fraction B had been hydrolysed, it yielded a sesquiterpene, with the sp. gr. 0·930 at 15° and α_D 0°45′ and boiling at 273—274° under the ordinary pressure. A. McK.

Caoutchouc Substances containing Oxygen. Paul Alexander (*Chem. Centr.*, 1904, ii, 705—706; from *Dresd. Gummi-Zeit.*, 18, 867—869. Compare Weber, this vol., i, 331).—Dry pontianac (Dead Borneo, Beck) contains 80 per cent. of substances soluble in acetone, of which the main component is a compound $C_{25}H_{40}O$, or more probably $C_{50}H_{80}O_2$. This substance melts at 161° and is the least soluble in acetone. The quantity of material insoluble in acetone never amounts to more than 15 per cent. of the dry pontianac. Analysis of the substance obtained after purifying a sample, which was more than 3 years old, by dissolving in chloroform and precipitating with ether, indicated the composition $C_{10}H_{16}$, and Weber's nitrogen dioxide additive product (*loc. cit.*) had the composition $C_{10}H_{16}O_4N_2$.

Guayrule caoutchouc, obtained from one of the Mexican *Compositæ*, was found to contain 60·3 per cent. of pure caoutchouc when tested by Weber's nitrogen dioxide method. The portion insoluble in acetone had the composition $C_{10}H_{16}$, but the nitrogen dioxide compound appeared to contain less carbon and hydrogen and more nitrogen than the normal additive product. The presence of caoutchouc substances rich in oxygen could not be detected. E. W. W.

Presence of Esters of Cinnamic Acid in Specimens of Gutta-percha. Pieter van Romburgh (*Ber.*, 1904, 37, 3440—3443). —Two esters of cinnamic acid have been isolated from the resin of crude gutta-percha obtained from *Palaquium calophyllum* from Java. The one ester melts at 145—149°, and the other, which is identical with Tschirch's crystalalban (this vol., i, 76), melts at 242° (corr.), and on hydrolysis yields cinnamic acid and an *alcohol* melting at 210°. The alcohol somewhat resembles cholesterol. Its *acetate* melts at 212° and its *benzoate* at 262°.

Other specimens of gutta-percha yield the same products, but that from *Payena Leerii* appears not to contain esters of cinnamic acid.

J. J. S.

Simple Mode of Preparing Synthetic Populin. Leonard Dobbin and Alex. D. White (*Pharm. J.*, 1904, [iv], 19, 233—234). —Populin (benzoylsalicin) can be readily synthesised by the action of benzoyl chloride on salicin in presence of aqueous potassium hydroxide according to the Schotten-Baumann method. E. G.

Saponin Substances. Rudolf Kobert (*Chem. Centr.*, 1904, ii, 450—451; from *Stuttgart. Verlag von Ferdinand Enke*, 1904. Compare Abstr., 1893, i, 424).—Saponin substances are more or less completely salted out by means of ammonium sulphate, the precipitation taking place more readily from warm solutions; quillajic acid and quillaja-

sapotoxin may be separated in this way, the former being completely precipitated, but not the latter. The Levantine sapotoxin is not identical with that of quillaja bark, since it is only partially precipitated by ammonium sulphate. Cyclamin from sow-bread, melanthin of *Nigella sativa*, chamælirin, sarsaponin, the neutral and acid saponins of guaiacum bark and leaves, polygalic acid of Senega root, and cereic acid are also precipitated by the sulphate.

Radix saponariæ rubræ contains two saponins, saporubric acid and saporubrin; the former is precipitated by ammonium sulphate, but not the latter. Other glucoside-substances, such as solanin, solanein, helleborein, ipecacuanhic acid, and condurangin are also precipitated by ammonium sulphate. When the saponins or sapogenins are salted out of solutions containing natural or artificial colouring matters, such as the dye contained in *Aplysia*, methylene-blue, neutral-red, methyl-violet, cyanin, &c., the dye is partly carried down by the precipitate; the colouring matter of blood is not, however, affected. Dyes are also extracted by aqueous solutions of the saponins and of condurangin through permeable membranes. The saponins resist the action of most animal enzymes, but are attacked by extracts of spiders, Russian tarantula, and dried ant pupæ with formation of a small quantity of sugar. When introduced into the blood in doses which are not fatal, the saponins do not, as a rule, cause hæmoglobinuria; cyclamin, parillin, sarsaponin, smilasaponin, monesin, and sapotin are exceptions, however, in this respect. Cyclamin also causes local coagulation of fibrin and thrombosis. The saponins which show the strongest hæmolytic action, when tested in glass vessels, also induce hæmoglobinuria most rapidly, but in the latter case the antitoxins of the serum play an important part. The hæmolytic action of each saponin on blood which has been diluted to 100 times its volume with sodium chloride solution has a certain value which is independent of the nature of the blood; guinea-pig blood is, however, especially sensitive.

The extraction of quillajic acid, polygalic acid, and the saponin acids of guaiacum from aqueous solutions by means of amyl or *iso*butyl alcohol is greatly facilitated by heating or by adding ammonium sulphate, but the extraction of sapotoxin is not affected. The saponin substances give the same reaction with ferric chloride and potassium ferricyanide as the corpse alkaloids, but in some cases only after warming. Quillajic acid and sapotoxin reduce warm ammoniacal solutions of silver or of gold chloride. The hæmolytic action of sapotoxin is due to its combination with the lecithin or cholesterol of the red corpuscles, and by this means causes the solution of the cells. These compounds may be prepared by heating the components in presence of water; the lecithin sapotoxin destroys the vitality of protoplasm and has a hæmolytic action, whilst the cholesterol compound is not poisonous.

When quillajic acid and sapotoxin are injected into the blood of rabbits in gradually increasing doses, the organism becomes immune to a certain limit. The saponin substances of quillaja bark have an effect on the muscular, but not on the nervous, system of the heart; living hearts of frogs, *Torpedo ocellata* and *Aplysia limacina* are quickly

killed. One part of quillajic acid or sapotoxin in 300,000 of sea water is sufficient to cause the death of fish; other animals are less affected, and crabs scarcely at all, the chitin membrane of the gills preventing the access of these compounds. Cholesterol sapotoxin is not poisonous even to fish. The acid is the only component of quillaja bark which has the same physiological action as the bark itself. Ten times the quantity of quillajic acid is required to cause death by subcutaneous injection in the case of frogs and other invertebrata as in the case of warm-blooded animals. Cephalopods are more affected by intravenous than by subcutaneous injection. Quillajic acid and sapotoxin act on the red corpuscles of the blood of bony and cartilaginous fish about as strongly as on those of ox-blood. For hæmolytic experiments, the blood may be diluted with a 3·5 per cent. solution of sodium chloride instead of with physiological sodium chloride solution. The white corpuscles of cephalopods, snails, crabs, and *Gephyreæ* are dissolved by saponin substances if the concentration of the latter is sufficiently great, solution being caused by the formation of lecithin and cholesterol compounds. The use of the poisonous saponin substances of quillaja bark and red soap-wort in the manufacture of aërated lemonade and in the preparation of cod-liver and castor-oil emulsions should be legally prevented; the harmless neutral saponins of guaiacum bark might be used as substitutes. E. W. W.

The Sugar of the Aloins. Eugène Léger (*J. Pharm. Chim.*, 1904, [vi], 20, 145—148. Compare Abstr., 1903, i, 356).—The aloins cannot be hydrolysed by means of dilute acids and soluble ferments, but when left in contact during prolonged periods with alcohol, resolution occurs with formation of a sugar. This compound, which has the properties of a pentose, is formed both by barbaloin and *iso*-barbaloin, and is named by the author *aloinose*. This result confirms the view that the aloins are glucosides, as previously suggested by the author. G. D. L.

Decomposition Products of Aloin. Otto A. Oesterle and Alexis Babel (*Chem. Centr.*, 1904, ii, 340; from *Schweiz. Woch. Pharm.*, 42, 329—332).—Tilden's aloexanthin (this Journal, 1877, ii, 267) is shown to be impure rhein, which according to Hesse is tetrahydroxymethylanthraquinone. It is totally different in its behaviour from Seel's tetrahydroxymethylanthraquinone (Abstr., 1901, i, 92). It is uncertain whether the aloechrysin (obtained from the impure rhein) stands in the same relation to rhein as Seel's hydrated methyltrihydroxyanthraquinone oxide to his tetrahydroxymethylanthraquinone. N. H. J. M.

Lactucon [Lactucerin]. Cæsar Pomeranz and F. Sperling (*Monatsh.*, 1904, 25, 785—792. Compare Kassner, Abstr., 1887, 605; Hesse, Abstr., 1888, 722).—Lactucerin, obtained from *Lactucarium Germanicum* by extraction with light petroleum and purified by treatment with ether and animal charcoal and by repeated recrystallisation from alcohol, has the molecular composition $C_{23}H_{36}O_2$, crystallises in

small needles, melts at 184°, has neither odour nor taste, has $[\alpha]_D + 50°$ at 18°, and is easily soluble in ether, benzene, chloroform, light petroleum, carbon disulphide, or hot alcohol, but is insoluble in water. When boiled with alcoholic potassium hydroxide, it is hydrolysed to acetic acid and *lactucol*, $C_{21}H_{34}O$, which crystallises in small, white needles, melts at 154·5°, and yields lactucerin when boiled with sodium acetate and acetic anhydride. The action of bromine on lactucerin in carbon disulphide solution leads to the formation of an *additive* product, $C_{23}H_{36}O_2Br_2$, which crystallises in small, yellow needles and decomposes when heated. G. Y.

Researches on Scammonin. PAUL REQUIER (*J. Pharm. Chim.*, 1904, [vi], 20, 148—151).—On lixiviation of scammony root with alcohol, it yields 7·2 per cent. of purified scammonin. The water used in washing the crude compound contains a lævorotatory tannin, giving an intense green coloration with ferric salts. The aqueous liquids also contain a dextrorotatory sugar, probably a pentose, and a nitrogen compound giving ammonia with potash and nitrogen with hypobromite. G. D. L.

Brazilin and Hæmatoxylin. VIII. JOSEF HERZIG and JACQUES POLLAK (*Monatsh.*, 1904, 25, 871—893. Compare Abstr., 1894, i, 341; 1896, i, 379; 1899, i, 381, 821; 1901, i, 478; 1902, i, 482; 1903, i, 270, 713; this vol., i, 333).—[With EUGEN G. GALITZENSTEIN.] —The isomeride of trimethylbrazilone can be titrated with a normal alkali with phenolphthalein as indicator; it is only partially precipitated, from its solution in an aqueous alkali hydroxide, on saturation with carbon dioxide, the remainder being precipitated unchanged on addition of a mineral acid. When warmed with potassium hydroxide and methyl iodide in alcoholic solution, or when treated with diazomethane, it forms the *methyl ether*, $C_{16}H_8O_2(OMe)_4$, which crystallises from alcohol, melts at 82—83°, remains unchanged when boiled with sodium acetate and acetic anhydride, but is hydrolysed to its parent substance, $C_{16}H_8O_2(OMe)_3 \cdot OH$, when treated with alcoholic or aqueous potassium hydroxide. No oxime could be obtained from the isomeride of trimethylbrazilone or from α-trimethyldehydrobrazilin.

The sulphate obtained by the action of sulphuric acid on triacetylbrazilein in glacial acetic acid solution is acetylated, with or without the presence of zinc dust, to triacetylbrazilein; when treated with water or sodium acetate solution, it is decomposed yielding an amorphous substance. When boiled with sodium acetate, zinc dust and glacial acetic acid for about half-an-hour, and again after addition of acetic anhydride, the sulphate yields tetra-acetylbrazilein. On hydrolysis with hydrogen chloride in alcoholic solution, tetra-acetylbrazilein yields a yellow, amorphous *substance*, which dissolves in aqueous alkalis to a colourless solution, which becomes red on boiling; on acetylation, without zinc dust, it forms tetra-acetylbrazilein.

[With BR. VOUK.]—Dinitrotetramethylhæmatoxylone does not form an acetyl derivative when boiled with sodium acetate and acetic anhydride (compare Gilbody and Perkin, Proc., 1899, 15, 27). When treated with potassium hydroxide in aqueous solution, it yields

6-nitrohomoveratrole, tetramethoxydinitrodibenzyl (Gilbody and Perkin, Trans., 1902, 81, 1049), and 2-carboxy-5 : 6-dimethoxyphenoxyacetic acid (Perkin and Yates, Trans., 1902, 81, 241). The *methyl* ester, $CO_2Me\cdot C_6H_2O(OMe)_2\cdot CH_2\cdot CO_2Me$, of the latter forms white crystals and melts at 84—87°. G. Y.

Hæmatein and Hæmalum. PAUL MAYER (*Chem. Centr.*, 1904, ii, 228; from *Zeit. wiss. Mikros.*, 20, 409—411).—Hæmatein is readily obtained by dissolving 1 gram of hæmatoxylin in 10 c.c. of boiling water, adding 0·2 gram of sodium iodate dissolved in 2 c.c. of water. The hæmatein is separated by filtration after 1 or 2 hours, washed with cold water, and dried at the ordinary temperature or with moderate heat. Brazilein is prepared in a similar manner. When alum (50 grams) is added to hæmatoxylin (1 gram) and sodium iodate (0·2 gram), hæmalum is obtained. Chloral hydrate and citric acid are added to enable it to be kept. N. H. J. M.

Probable Identity of Phylloerythrin and Cholehæmatin. LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1904, 6, 276—280).—The spectroscopic examination of chloroform solutions of phylloerythrin and cholehæmatin reveals four absorption bands in the visible part of the spectrum, which, in regard to position and relative intensity, appear to be identical. The two bands in the ultra-violet differ somewhat, but this is probably due to impurities in the cholehæmatin solution employed, and the identity of the two substances seems very probable. H. M. D.

Colouring Matters of Rosa Gallica. WILLIAM A. H. NAYLOR and E. J. CHAPPEL (*Pharm. J.*, 1904, [iv], 19, 231—233).—The petals of *Rosa gallica* contain two colouring matters, one yellow, the other red. The yellow colouring matter, $C_{15}H_{12}O_6$, crystallises from dilute alcohol in minute needles, does not melt when heated to 220°, gives a brownish-black coloration with ferric chloride, and an orange-red precipitate with lead acetate; it slowly reduces boiling Fehling's solution, and imparts an orange-yellow coloration with a green fluorescence to warm sulphuric acid. This substance is not identical with quercitrin, as was supposed by Filhol (*Rep. Pharm.*, 1863). When heated with potassium hydroxide at 210—230°, it yields phloroglucinol and another substance which is probably protocatechuic acid. The yellow colouring matter is hydrolysed with difficulty by sulphuric or hydrochloric acid, red amorphous products being formed.

The red colouring matter was obtained as a deep red, amorphous powder, soluble in water or alcohol. The crystalline alkali salts of this substance described by Senier (Abstr., 1877, ii, 502) could not be obtained. E. G.

Behaviour of Wool Fibre to Certain Acid Dyes. Contribution to the Theory of Dyeing. EDMUND KNECHT (*Ber.*, 1904, 37, 3479—3484. Compare Abstr., 1889, 49, 869).—Experiments made with orange G and crystal-ponceau, ponceau 2G and xylidine-

ponceau, orange II and "Echt" red A, "Echt" acid fuchsin B, the corresponding naphthylamine dye, picric acid, *s*-trinitrocresol, and *s*-trinitroxylenol indicate that the amounts of dye taken up by the wool fibre are in the ratios of the molecular weights of the dyes.

The amount of dye taken up does not vary much with the amount of water present. The actual amount taken up was determined by estimating the amount originally present in solution and then the amount left after dyeing. All estimations were made by aid of titanium trichloride. This method, however, did not yield good results with trinitrocresol and trinitroxylenol.

In the case of crystal-ponceau, the curve representing the relationship between amount of dye (in per cent.) present and amount taken up by the fibre is represented by a straight line until 17 per cent. has been taken up, and then rises rapidly and runs nearly parallel with the vertical ordinate. J. J. S.

Formation of Furoyl Derivatives by means of Pyromucic Chloride. Synthesis of Pyromykuric Acid. ERICH BAUM (*Ber.*, 1904, 37, 2949—2961).—A number of furoyl compounds have been prepared by the action of pyromucic chloride on phenols, amines, and amino-acids in aqueous alkali hydroxide or carbonate, or in pyridine solution. The reaction does not take place with methylamine. The resulting products resemble the corresponding benzoyl compounds, than which they are usually more soluble. The furoyl compounds are easily hydrolysed by boiling with barium hydroxide in aqueous solution; hydrolysis, by means of boiling hydrochloric acid, is usually accompanied by further decomposition.

Pyromykuric acid (Jaffé and Cohn, Abstr., 1887, 1032) is formed by the action of pyromucic chloride on glycine in slightly alkaline solution. The *ethyl* ester crystallises in long, white, silky needles and melts at 77°.

The following new compounds are described; the temperatures given are melting points:—

Phenyl pyromucate, $C_4OH_3 \cdot CO_2Ph$, crystallises in prisms, 41·5°; m-*phenylene dipyromucate*, $C_6H_4(C_5H_3O_3)_2$, crystallises in nacreous plates, 128—129°. *Difuroylhydroxamic acid*, $(C_4OH_3 \cdot CO)_2N \cdot OH$, crystallises in prisms, 180°; when heated with an alkali hydroxide and neutralised, it gives a dark violet coloration with ferric chloride. *Furoylpiperidide*, $C_5H_3O_2 \cdot C_5H_{10}N$, crystallises in glistening, brittle rhombohedra, 58°; *ethylenedifuramide* crystallises in white prisms, 200°; *furoyl*-p-*toluide* forms glistening prisms, 107·5°; *furoyl*-m-*toluidide* crystallises in glistening prisms, 87°; *furoyl*-o-*toluidide* separates from petroleum in long, glistening needles, 62°. *Furoylalanine*, $C_5H_3O_2 \cdot C_3H_6O_2N$, forms glistening, hexagonal plates, 169°; the *barium* $(C_8H_8O_4N)_2Ba$, and the *silver*, $C_8H_8O_4NAg$, salts are described; the *ethyl* ester, $C_8H_8O_4NEt$, crystallises in small, hexagonal plates, 71—72°. *Furoyl*-l-*aspartic acid*, $C_5H_8O_2,C_4H_6O_4N$, forms four-sided prisms, 162—163°, $[\alpha]_D$ +43·17° at 20°. *Furoyl*-l-*asparagine* crystallises in colourless prisms, 172—173°, $[\alpha]_D$ +19·75° at 20°; the *barium*, $(C_9H_9O_5N_2)_2Ba,2H_2O$, the *copper*, $(C_9H_9O_5N_2)_2Cu,H_2O$, and the silver, $C_9H_9O_5N_2Ag$, salts are described. *Phenylpyromykuric acid*, $C_{13}H_{11}O_4N$,

formed from α-phenylaminoacetic acid, crystallises in clusters of slender, white needles, 178—179°; the *barium* salt, $(C_{13}H_{10}O_4N_2)_2Ba$, crystallises in prisms. G. Y.

A Second Synthesis of Chrysin. STANISLAUS VON KOSTANECKI and VICTOR LAMPE (*Ber.*, 1904, 37, 3167—3168. Compare Fainberg and Kostanecki, this vol., i, 682; Kostanecki and Tambor, this vol., i, 426; Kostanecki, Lampe, and Tambor, this vol., i, 763).—3 : 6 : 8-*Tribromo*-5 : 7-*dimethoxyflavanone*, $\begin{matrix} C(OMe){:}CBr{\cdot}C{-}O{-}CHPh \\ CBr{:}C(OMe){\cdot}C{\cdot}CO{\cdot}CHBr \end{matrix}$, prepared by brominating 5 : 7-dimethoxyflavanone, crystallises from benzene in prisms and melts and decomposes at 174—175°. When boiled with alcoholic potassium hydroxide, it yields 6 : 8-*dibromo*-5 : 7-*dimethoxyflavone*, $\begin{matrix} C(OMe){:}CBr{\cdot}C{-}O{-}CPh \\ CBr{:}C(OMe){\cdot}C{\cdot}CO{\cdot}CH \end{matrix}$, which separates from a mixture of glacial acetic acid and ethyl alcohol in needles and melts at 253°. When the latter compound is boiled with hydriodic acid, it forms 5 : 7-dihydroxyflavone (chrysin), $\begin{matrix} C(OH){:}CH{\cdot}C{-}O{-}CPh \\ CH{:}C(OH){\cdot}C{\cdot}CO{\cdot}CH \end{matrix}$. A. McK.

Flavindogenides. A. KATSCHALOWSKY and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, 37, 3169—3172).—The methylene group in flavanone, $C_6H_4{<}\begin{matrix} O{-}CHPh \\ CO{\cdot}CH_2 \end{matrix}$, is very reactive on account of its proximity to the carbonyl group, and reacts readily with bromine and with nitrous acid to form 3-bromoflavanone and *iso*nitrosoflavanone respectively. It is now shown that the hydrogen atoms of this methylene group may be replaced by aldehyde groups to form compounds analogous to indogenides, oxindogenides, deoxycarbindogenides, and carbindogenides, and which are termed flavindogenides. They are prepared by saturating a hot alcoholic solution of a mixture of flavanone and aldehyde with hydrogen chloride and then adding water, when the dye separates and may be crystallised from alcohol.

From 6-ethoxyflavanone, $\begin{matrix} CH{:}CH{\cdot}C{-}O{-}CHPh \\ OEt{\cdot}C{=}CH{\cdot}C{\cdot}CO{\cdot}CH_2 \end{matrix}$, the following compounds were prepared:

6-*Ethoxy*-3-*benzylideneflavanone*, $OEt{\cdot}C_6H_3{<}\begin{matrix} O{-}CHPh \\ CO{\cdot}C{:}CHPh \end{matrix}$, which separates from alcohol in leaflets and melts at 106°.

6-*Ethoxy*-3-*anisylideneflavanone* separates in spear-shaped crystals and forms a magenta solution with concentrated sulphuric acid.

6-*Ethoxy*-3-*veratrylideneflavanone* crystallises in pyramids, melts at 145—146°, and forms a violet solution with concentrated sulphuric acid.

By the action of piperonal on 6 : 2′-dimethoxyflavanone, 6 : 2′-*dimethoxy*-3-*piperonylideneflavanone*,

$$OMe{\cdot}C_6H_3{<}\begin{matrix} O{-}CH{\cdot}C_6H_4{\cdot}OMe \\ CO{\cdot}C{=}CH{-}C_6H_3{<}\begin{matrix} O \\ O \end{matrix}{>}CH_2, \end{matrix}$$

is formed; this separates in yellow prisms, melts at 207—209°, and yields a violet-red coloration with concentrated sulphuric acid.

7 : 8-*Dimethoxy-3-anisylideneflavanone* forms tiny plates, melts at 186°, and gives an orange coloration with concentrated sulphuric acid.

7 : 8-*Dimethoxy-3-veratrylideneflavanone* forms tiny plates, melts at 196°, and gives a red coloration with concentrated sulphuric acid.

7 : 8-*Dimethoxy-3-piperonylideneflavanone* separates from alcohol in pyramids, melts at 185°, and gives a magenta coloration with concentrated sulphuric acid. A. McK.

Xanthonium and Thioxanthonium Compounds. HANS BÜNZLY and HERMAN DECKER (*Ber.*, 1904, **37**, 2931—2938. Compare Abstr., 1900, ii, 518; 1902, i, 50; this vol., i, 344).—Xanthonium and thioxanthonium compounds may be prepared by Grignard's reaction, and show a complete parallelism in properties and chemical behaviour with acridinium compounds. They are of interest as containing quadrivalent oxygen or sulphur, combined with three carbon-valencies.

Phenylxanthenol (*carbinol* form of *phenylxanthonium hydroxide*), $C_6H_4<\underset{O}{\overset{CPh(OH)}{\rule{2em}{0.4pt}}}>C_6H_4$, prepared by heating xanthone in benzene solution with magnesium phenyl bromide, forms colourless prisms and melts at 158·5—159°. It sublimes without decomposition and dissolves readily in chloroform or benzene, sparingly in light petroleum. The *ethyl ether* forms terrace-like crystals and melts at 102—103°; the *methyl ether* forms colourless needles and melts at 96—97°.

The carbinol dissolves in mineral acids to orange-red solutions, becoming slowly paler on dilution with water, the carbinol being precipitated. Heating favours the formation of the oxonium modifications.

Phenylxanthonium ferrichloride, $C_{19}H_{13}OCl,FeCl_3$, forms glistening, reddish-brown scales and melts at about 174°. The *mercurichloride* forms large, red prisms and begins to melt at about 230°, decomposing at 235°. The *cadmiobromide* forms purple plates; the *aurichloride* forms golden needles. These salts are stable in air and are hydrolysed by warm water. Bromine water precipitates *phenylxanthonium tribromide* from solutions of xanthonium salts, forming red scales, melting and decomposing at 168—170°. The *tri-iodide* forms glistening, black needles and dissolves in chloroform or glacial acetic acid to dark violet solutions.

[With C. WITTMANN.]—*Phenylthioxanthenol* (*carbinol* form of *phenylthioxanthonium hydroxide*), $C_6H_4<\underset{S}{\overset{CPh(OH)}{\rule{2em}{0.4pt}}}>C_6H_4$, from thioxanthone and magnesium phenyl bromide, separates from benzene and light petroleum in compact, drusy masses and melts at 105—106°. The *ethyl ether* forms thick crystals and melts at 76—77°.

Phenylthioxanthonium salts form intensely red solutions and are more stable than the corresponding oxonium salts. The *ferrichloride* forms dark red needles and melts at 169°; the *cadmiobromide* forms

broad, dark red needles, and the *mercurichloride* dark red prisms. The *tribromide* forms dark red needles and melts at about 180°.

C. H. D.

Constitution of Trihydroxytetramethylfluorone. FRANZ WENZEL and A. SCHREIER (*Monatsh.*, 1904, 25, 657—681. Compare Abstr., 1900, i, 308; this vol., i, 518).—When heated together at 140—150° in glacial acetic acid solution, in presence of concentrated sulphuric acid, dimethylphloroglucinol and 2 : 4 : 6-trihydroxy-3 : 5-dimethylbenzaldehyde form a dark red solution, which gradually deposits an additive compound of 1 : 3 : 8-trihydroxy-2 : 4 : 5 : 7-tetramethylfluorone and sulphuric acid, $C_{17}H_{16}O_5,H_2SO_4$. This crystallises in delicate, glistening, matted, red needles, decomposes when heated, is stable towards alcohol, but loses sulphuric acid when treated with water. If the condensation takes place in presence of hydrochloric acid, the additive *compound* with hydrochloric acid is obtained. This is also formed as a by-product in the formation of trihydroxydimethylbenzaldehyde by the action of hydrogen chloride on dimethylphloroglucinol and hydrocyanic acid. It crystallises in slender, glistening, red needles and yields trihydroxytetramethylfluorone on prolonged boiling with alcohol.

The compound $C_{17}H_{16}O_5,H_2SO_4$ is also formed when methylenebisdimethylphloroglucinol (Böhm, Abstr., 1902, i, 39) is warmed with concentrated sulphuric acid.

1 : 3 : 8-Trihydroxy-2 : 4 : 5 : 7-tetramethylfluorone,

$$\begin{array}{l} \mathrm{CMe{=}C(OH){\cdot}C{\cdot}CH{:}C{\cdot}C(OH){:}CMe} \\ \mathrm{C(OH){:}CMe{-}C{-}O{-}C{=}CMe{-}CO} \end{array},$$

crystallises from resorcinol in long, blood-red needles, from acetic acid in dark red plates; like its acid additive compounds, when heated, it decomposes without melting; it is only very slightly soluble in alcohol or glacial acetic acid.

The action of acetic anhydride on methylenebisdimethylphloroglucinol leads to the formation of a *hexa-acetyl* derivative,

$$C_6Me_2(OAc)_3{\cdot}CH_2{\cdot}C_6Me_2(OAc)_3,$$

which crystallises in white leaflets, melts at 232—233°, and, on hydrolysis with concentrated sulphuric acid, yields trihydroxytetramethylfluorone.

Reduction of trihydroxytetramethylfluorone with sodium amalgam and water leads to the formation of tetrahydroxytetramethylxanthen, $\begin{array}{l} \mathrm{CMe{:}C(OH){\cdot}C{\cdot}CH_2{\cdot}C{\cdot}C(OH){:}CMe} \\ \mathrm{C(OH){:}CMe{\cdot}C{-}O{-}C{-}CMe{:}C{\cdot}OH} \end{array}$, which crystallises in clusters of white needles, melts at 320—324°, and is soluble in alcohol, acetone, or ether. When dry, it is comparatively stable, but when moist it is rapidly oxidised; with ferric chloride, it gives a dark red coloration, and when warmed with sulphuric acid it is converted, but less easily than methylenebisdimethylphloroglucinol, into the sulphuric acid compound of trihydroxytetramethylfluorone. The *tetra-acetyl* derivative of tetrahydroxytetramethylxanthen crystallises in white needles, melts at 268—270°, and forms a fluorescent solution in concentrated

sulphuric acid. This acetyl compound is oxidised by chromic acid in glacial acetic acid solution to the *tetra-acetyl* derivative of tetrahydroxytetramethylxanthydrol, $C_6Me_2(OAc)_2<\underset{O}{\overset{CH(OH)}{\rule{2em}{0.4pt}}}>C_6Me_2(OAc)_2$, which is also formed by the action of acetic anhydride and sodium acetate on 1 : 3 : 8-trihydroxy-2 : 4 : 5 : 7-tetramethylfluorone. It melts at 256—259°, and is reduced by zinc dust in glacial acetic acid solution to tetra-acetoxytetramethylxanthen.

The action of bromine on trihydroxytetramethylfluorone in methyl-alcoholic solution leads to the formation of a *bromo*-derivative,

$$C_{17}H_{15}O_5Br,$$

which crystallises in dark red needles, and of the *methyl ether* of tetrabromotetramethyltetraketo-octohydroxanthydrol,

$$\begin{array}{l} \text{CMeBr·CO·CBr·CH(OMe)·C·CO——CMeBr} \\ \text{CO——CMe:C————O————C·CMeBr·CO} \end{array},$$

which forms large, almost white crystals, which become yellow on exposure to air, red on exposure to light. It melts and decomposes at 155—160° and is only slightly soluble in methyl or ethyl alcohols, but easily so in benzene or glacial acetic acid.

As the condensation of dimethylphloroglucinol and 2 : 4 : 6-trihydroxy-3 : 5-dimethylbenzaldehyde can take place only in one way, the experimental details now published confirm the fluorone constitution ascribed to the condensation products of salicylaldehyde and the homologues of phloroglucinol. G. Y.

The Indophenine Reaction. Franz W. Bauer (*Ber.*, 1904, 37, 3128—3130. Compare Bauer, this vol., i, 519).—A reply to Storch (this vol., i, 610) and to Liebermann and Pleus (this vol., i, 684). A. McK.

Indophenines. Heinrich Oster (*Ber.*, 1904, 37, 3348—3352).—With ordinary substituted indophenines, as also with the analogous compounds which are formed from phthaloneimide and thiophen or from thiophthen and isatin, the mechanism of formation is identical, water being eliminated in every case (compare Bauer, this vol., i, 519; Liebermann and Pleus, this vol., i, 684). Thiophthen forms two distinct indophthenines according as it is combined with 1 or with 2 molecules of isatin. All indophenines form blue solutions with concentrated sulphuric acid.

Nitroindophenine, $NO_2·C_8H_3ON·C_4SH_3$, prepared from nitroisatin and thiophen, is a dark blue powder, which forms a bright blue solution with concentrated sulphuric acid.

Carbindophenine, $C_9H_4O_2N·C_4SH_3$, prepared from phthaloneimide and thiophen, is dark blue and forms a blue solution with concentrated sulphuric acid.

Monoisatinindophthenine, $C_8H_4ON·C_6S_2H_3$, prepared by adding concentrated sulphuric acid to a solution of equal weights of isatin and thiophthen in glacial acetic acid, is a grey powder, which forms a reddish-blue solution with concentrated sulphuric acid; on exposure to light, it gradually becomes brown.

Di-isatinindophthenine, $C_6S_2H_2(C_8H_4ON)_2$, prepared by the action of

concentrated sulphuric acid on a solution of thiophthen (1 part) and isatin (3 parts) in glacial acetic acid, is a blue powder.

Bromoindophthenine, $C_8H_3ONBr \cdot C_6H_3S_2$, is a grey powder. *Carbindophthenin*, $C_9H_4O_2N \cdot C_6H_3S_2$, prepared from phthaloneimide and thiophthen, is a bright green powder. Phenanthraquinone and thiophen form a *compound*, $C_{18}H_{10}OS$, which separates in deep green flakes; the corresponding *compound*, $C_{20}H_{10}OS_2$, with thiophthen is a bright green powder. A. McK.

Caffearine, an Alkaloid from Coffee. L. Graf (*Zeit. öffentl. Chem.*, 1904, 15, 279—281).—The existence of this alkaloid, which was isolated from coffee by Palladino (Abstr., 1894, i, 214; 1895, i, 629), having been doubted recently, the author states that having repeated Palladino's experiments he has succeeded in obtaining the alkaloid in a pure state. It may also be obtained in small quantities from aqueous infusions of raw coffee beans without using calcium hydroxide. Caffeine and proteids, when treated with the latter substance, do not yield caffearine. L. de K.

***iso*Cinchonine Bases.** Zdenko H. Skraup and Rudolf Zwerger (*Monatsh.*, 1904, 25, 894—906. Compare Abstr., 1903, i, 715).—When warmed on the water-bath with concentrated hydrochloric acid, α-*iso*cinchonine yields a small amount of the sparingly soluble hydrochloride of hydrochlorocinchonine. The action of a saturated aqueous solution of hydrogen chloride on α-*iso*cinchonine in a sealed tube at 100°, leads to the formation of trihydrochlorocinchonine, the sparingly soluble hydrochloride of hydrochlorocinchonine, and a *hydrochloride* which is easily soluble in water, and, with ammonia, yields hydrochloro-α-*iso*cinchonine, $C_{19}H_{23}ON_2Cl$, which crystallises in microscopic prisms and melts at 185—186°; the *sulphate*,

$$(C_{19}H_{23}ON_2Cl)_2,H_2SO_4,4H_2O,$$

crystallises in microscopic prisms, loses $4H_2O$ at 105°, and is sparingly soluble in water (Hesse, Abstr., 1893, i, 677). Hydrochloro-α-*iso*cinchonine is also formed, along with hydrochlorocinchonine, by the action of concentrated hydrochloric acid on trichlorocinchonine at 100° under pressure. When the sparingly soluble sulphate is heated with alcoholic potassium hydroxide, it yields a base which melts at 247—248° and may be cinchonine.

The action of hydrochloric acid on β-*iso*cinchonine and on *allo*cinchonine leads to the formation of traces of hydrochlorocinchonine only. When warmed with saturated hydrobromic acid, α-*iso*cinchonine yields the hydrobromide of hydrobromocinchonine.

α- and β-*iso*Cinchonines do not enter into reaction with chlorine in hydrochloric acid solution. Cinchonine forms an additive compound with chlorine, $C_{19}H_{22}ON_2Cl_2$, which melts at 217—218° (Koenigs, Abstr., 1892, 1011). A base of the same composition, which melts at 205—206° and is possibly identical with cinchonine dichloride, is formed by the action of chlorine on *allo*cinchonine. G. Y.

Attempts to prepare Alkaloids of the *iso*Quinoline Series. Martin Freund (*Ber.*, 1904, 37, 3334—3337. Compare Liebermann and Glawe, this vol., i, 765).—α-Substituted derivatives of hydrocotar-

nine may be prepared by the application of Grignard's reaction to cotarnine or to its salts, such as the hydrochloride or cyanide. Dihydrocotarnine, melting at 163—164°, may be prepared by Grignard's reaction with cotarnine, using ethylene bromide, methylene chloride, benzylidene chloride, or acetylene tetrachloride respectively. Hydrastinine behaves like cotarnine in these reactions.

By the application of Grignard's reaction to berberinal, α-derivatives of a dihydroberberine are formed; *benzyldihydroberberine* forms yellow rhombohedra and melts at 161—162°.

Anhydrocotarnine benzyl cyanide melts at 134° to a red liquid; its *hydrochloride* melts at 154—155°.

Anhydrocotarnine benzyl cyanide-methine methiodide,

$$CH_2{:}O_2{:}C_6H(OMe)(CH{:}CPh{\cdot}CN){\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3I,$$

separates from alcohol in plates and melts at 225—227°; trimethylamine is formed by warming it with alkali. A. McK.

Morphine. V. New Basic Products from Methylmorphimethine: Tetramethylethylenediamine and Dimethylaminoethyl Ether. LUDWIG KNORR (*Ber.*, 1904, 37, 3494—3498. Compare Abstr., 1903, i, 849).—Hydrogen chloride reacts with methylmorphimethine, probably forming in the first place chloroethyldimethylamine (Abstr., 1894, i, 430; and this vol., i, 854). In place of this base, however, a mixture of ethanoldimethylamine and tetramethylethylenediamine is obtained. The *platinichloride* of the latter base crystallises in characteristic, glistening leaflets, and blackens and decomposes at 250°; the *aurichloride* forms small needles and melts and decomposes at 212°; the *picrate* crystallises in needles and melts at 197°.

Sodium ethoxide decomposes methylmorphimethine, forming methylmorphol and *dimethylaminoethyl ether*, $NMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$. The *aurichloride* forms flat, glistening lozenges, melting at 85—90°, and dissolves in hot water; the *picrate* crystallises from hot water in leaflets and melts at 119—121°; the *methiodide* (choline hydriodide ethyl ether) forms short prisms and melts at 160—165°.

Codeine methiodide and sodium ethoxide yield the same products, together with dimethylamine. C. H. D.

Morphine. VI. Dimethylaminoethyl Ether as a Decomposition Product from Thebaine Methiodide and Codeinone Methiodide. LUDWIG KNORR (*Ber.*, 1904, 37, 3499—3504).—Thebaine methiodide reacts readily with sodium ethoxide on warming to form thebaol and tetramethylethylenediamine (compare Freund, Abstr., 1897, i, 495). Thebaine methiodide is also decomposed on heating with alcohol at 160—165°, forming thebaol and dimethylaminoethyl ether, together with a small quantity of dimethylamine.

Alcohol also decomposes codeinone methiodide at 150—160°, yielding dimethylaminoethyl ether and 4 : 6-dihydroxy-3-methoxyphenanthrene, the latter being isolated in the form of its acetyl derivative.

The primary product in these cases is probably dimethylvinylamine, which, however, has not yet been prepared. At the moment of

formation, it combines with alcohol, forming dimethylaminoethyl ether. In similar manner, in the decomposition by acetic anhydride (Abstr., 1903, i, 849), the hydramine acetate is formed from the vinyl base. The tetramethylethylenediamine obtained above results from the combination of the vinyl base with dimethylamine.

The author's former assumption, that morphine contains an oxazine ring, is probably incorrect, and morphine and thebaine must be regarded as containing an oxygen bridge, $C_6H_3 \overset{\text{—O—}}{\underset{\text{CH:CH}}{\rightleftharpoons}} C_6H_3$, such as has been found in morphenol derivatives by Vongerichten (Abstr., 1900, i, 248). C. H. D.

Papaverine. MARTIN FREUND and HEINRICH BECK (*Ber.*, 1904, 37, 3321—3324).—When papaveraldine (Goldschmiedt, Abstr., 1886, 478) in the form of its sulphate is subjected to electrolytic reduction, using a leaden cathode, a secondary amine, $C_{20}H_{25}O_4N$, iso*tetrahydropapaverine*, is obtained. It is best isolated in the form of the *nitrosoamine*, which melts at 138°. The *hydriodide*, $C_{20}H_{25}O_4N,HI$, crystallises from alcohol in colourless prisms, which sinter at 245° and melt at 255°. The free base has only been obtained as a syrup. Its physiological properties have been examined. J. J. S.

Constitution of Sparteine. RUDOLF WACKERNAGEL and RICHARD WOLFFENSTEIN (*Ber.*, 1904, 37, 3238—3244).—Sparteine, $C_{15}H_{26}N_2$, can under no conditions be reduced, and is not therefore an unsaturated base, as Ahrens (Abstr., 1897, i, 231) claimed. Hydrogen peroxide converts it into sparteine oxide, melting at 127—128°, in which the oxygen is doubly linked to nitrogen. Further, sparteine contains no methyl group attached to nitrogen, as supposed by Ahrens. The authors consider it to be a dicyclic saturated ring system, one nitrogen being in a pyridine and one in a pyrrolidine ring. It boils at 326°, forms a *picrate* melting at 199—200°, a *platinichloride* decomposing at 244—257°, an *aurichloride* decomposing at 175—184°, a *hydriodide* melting at 226—228°, a *dihydriodide* melting at 257—258°, an *oxalate* crystallising with a molecule of alcohol and melting at 138—140°, and a *methobromide* melting and decomposing at 219°. E. F. A.

Synthesis of Polypeptides. V. Derivatives of Prolin (Pyrrolidine-2-carboxylic Acid). EMIL FISCHER and EMIL ABDERHALDEN (*Ber.*, 1904, 37, 3071—3075. Compare Abstr., 1903, i, 465, 799, 607, 800; this vol., i, 652).—The proline used was derived from gelatin and the method of isolation is described in detail. *a-Bromo*iso*hexoylprolin* (inactive), $CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot C_4NH_7\cdot CO_2H$, prepared by condensing the constituents in presence of normal sodium hydroxide, crystallises from acetone in colourless needles melting at 163° (corr.). The active bromo*iso*hexoylproline prepared from *l*-proline melts at 154—158° (corr.) and crystallises from acetone in microscopic prisms.

Leucylproline, $CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot C_4NH_7\cdot CO_2H$, formed by

the action of aqueous ammonia on the bromo-derivative, crystallises from ethyl acetate in aggregates of needles, melts between 116° and 119° (corr.), is easily soluble in water, and has a bitter taste. On heating at 145°, water is eliminated and *leucylprolinanhydride* is formed; this crystallises from water in minute needles melting between 117° and 121° (corr.). E. F. A.

A New Method for breaking down Cyclic Amines. JULIUS VON BRAUN (*Ber.*, 1904, 37, 2915—2922).—The action of phosphorus pentachloride on aromatic acylamines (this vol., i, 731) may be employed to break down the ring, producing either chlorinated primary amines or dichlorinated hydrocarbons.

Benzoylpiperidine reacts with phosphorus pentachloride at 120°, forming the imide chloride, $CClPh\colon N\cdot[CH_2]_5\cdot Cl$. On decomposing with water, distilling with steam, and then distilling the residue under reduced pressure, *benzoyl-ε-chloroamylamine*, $COPh\cdot NH\cdot[CH_2]_5\cdot Cl$, is obtained in white crystals melting at 66°. Hydrochloric acid hydrolyses it at 170—180° to ε-chloroamylamine (Gabriel, Abstr., 1892, 717).

If the benzoylpiperidine and phosphorus pentachloride are heated until the reaction ceases and the phosphorus oxychloride is removed by distillation, the residue may be distilled under reduced pressure, and consists of benzonitrile and αε-dichloropentane. The former may be removed by hydrolysis with hydrochloric acid.

αε-Dichloropentane is a colourless liquid, boiling and slightly decomposing at 176—178° and boiling at 79—80° under 21 mm. pressure. Benzylamine converts it into benzylamine hydrochloride and benzylpiperidine, $C_5H_{10}Cl_2 + 3C_7H_7\cdot NH_2 = C_5H_{10}N\cdot C_7H_7 + 2C_7H_7\cdot NH_3\cdot Cl$.

Benzoyltetrahydroquinoline reacts with phosphorus pentachloride to form the imide chloride only, a further fission being impossible. *o-γ-Chloropropylbenzanilide*, $COPh\cdot NH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CH_2Cl$, forms white crystals and melts at 108°, decomposing at a higher temperature. C. H. D.

Action of Bromine on Trichloropyrrole. Chlorobromomaleimide. VII. GIROLAMO MAZZARA and A. BORGO (*Gazzetta*, 1904, 34, ii, 125—128. Compare Abstr., 1902, i, 820; 1903, i, 51, 274; this vol., i, 614, 770, 771).—*Chlorobromomaleimide*,

$$\begin{matrix} CCl\cdot CO \\ | \\ CBr\cdot CO \end{matrix}\!\!>\!NH,$$

prepared by the action of bromine on an acetic acid solution of trichloropyrrole, separates from benzene in pale, lemon-yellow prisms melting at 196°. In aqueous solution, it yields a white, crystalline precipitate with ammoniacal silver nitrate solution.

On comparing the melting points of the halogen derivatives of maleimide and methylmaleimide, it is found that the mono-haloid derivatives of maleimide melt at about 50° higher than the corresponding compounds of methylmaleimide, whilst in the case of the dihaloid derivatives the difference in melting point is about 100°. T. H. P.

Action of Sulphuryl Chloride and Bromine on Pyrrole. VIII. GIROLAMO MAZZARA (*Gazzetta*, 1904, 34, ii, 178—184. Compare preceding abstract).—*Trichloromonobromopyrrole*,

$$\begin{matrix} CCl{:}CCl \\ | \\ CBr{:}CCl \end{matrix} > NH,$$

prepared by the action of bromine and sulphuryl chloride on an ethereal solution of pyrrole at 0°, separates from light petroleum in colourless, monoclinic prisms which have a yellowish-red reflex; it begins to turn brown at 105° and melts and decomposes at 115°. It has the normal molecular weight in freezing benzene. Oxidation with fuming nitric acid or bromine yields chlorobromomaleimide.

T. H. P.

Condensation of Ethyl Cyanoacetate with some Dihydroxyphenolic Aldehydes. II. GALEAZZO PICCININI (*Atti R. Accad. Torino*, 1903—1904, 39, 1024—1045. Compare this vol., i, 91 and 504).—With protocatechualdehyde, vanillin, and veratraldehyde, condensation with ethyl cyanoacetate and ammonia yields γ-substituted dicyanoglutaconimides [dicyanodihydropyridones], although in smaller proportions than in the other cases examined. The ammonium salt obtained with protocatechualdehyde is formed in two modifications, but their isomeric relations have not been determined.

The condensation of ethyl cyanoacetate with vanillin in presence of ammonia yields: (1) the *ammonium* salt of 3 : 5-*dicyano*-2-*hydroxy*-4-p-*hydroxy*-m-*methoxyphenyldihydro*-6-*pyridone*,

$$OH\cdot C_6H_3(OMe)\cdot C \lessdot \begin{matrix} C(CN)\cdot CO\text{———} \\ CH(CN)\cdot C(ONH_4) \end{matrix} \gtrdot N,$$

which crystallises from water in colourless flocculi containing $2\frac{1}{2}H_2O$, of which $1\frac{1}{2}$ mols. are lost in a vacuum over sulphuric acid; it begins to turn brown at 250°, but does not melt at 300°; when suspended in water in presence of bromine vapour, it gives a red coloration which, on adding a little ammonia solution, turns green, this gradually changing back to the red. (2) p-*Hydroxy*-m-*methoxybenzylidenecyanoacetamide*, $OH\cdot C_6H_3(OMe)\cdot CH{:}C(CN)\cdot CO\cdot NH_2$, which separates from 60 per cent. alcohol in yellow crystals melting at 210—210·5°; it remains unchanged on boiling with milk of magnesia, but yields ammonia when treated with cold lime-water; when boiled with excess of barium hydroxide, it yields vanillin, malonic acid, and ammonia, thus: $OMe\cdot C_6H_3(OH)\cdot CH{:}C(CN)\cdot CO\cdot NH_2 + 4H_2O = OMe\cdot C_6H_3(OH)\cdot CHO + CH_2(CO_2H)_2 + 2NH_3$.

The above ammonium salt and unsaturated amide are formed in the condensation of cyanoacetamide with vanillin in presence of ammonia.

The condensation of ethyl cyanoacetate with protocatechualdehyde in presence of ammonia yields: (1) The *ammonium* derivative of 3 : 5-*dicyano*-2 : 6-*diketo*-4-m-p-*dihydroxyphenyldihydropyridine*,

$$ONH_4\cdot C_6H_3(OH)\cdot C \lessdot \begin{matrix} C(CN)\text{—}CO \\ CH(CN)\cdot CO \end{matrix} > NH,$$

which is formed in two modifications. The α-salt ($+H_2O$), obtained in small proportion, crystallises from water in tufts of minute, colourless needles. Decomposition of the corresponding lead salt with

sulphuric acid yields the free compound, which separates from water in silky, white crystals ($+2H_2O$), turning brown at 250° but not melting at 300°. The β-salt ($+H_2O$), which constitutes the main bulk of the ammonium derivative, crystallises from water in slender, but rather heavy, prisms; the corresponding *barium* salt,

$$(C_{18}H_6O_4N_3)_2Ba+4H_2O,$$

crystallises from aqueous solution in silky, white needles. (2) 3 : 4-*Dihydroxybenzylidenecyanoacetamide*,

$$C_6H_3(OH_2)\cdot CH\dot{:}C(CN)\cdot CO\cdot NH_2,$$

which separates from water or alcohol in intensely yellow, shining prisms, commencing to turn brown at 210° and melting and decomposing at 232°. Its aqueous solution has an acid reaction to litmus, colours ferric chloride green and alkaline hydroxides red, and reduces ammoniacal silver nitrate solution. This compound is formed without the above ammonium derivative when protocatechualdehyde is condensed with cyanoacetamide and ammonia.

The condensation of ethyl cyanoacetate with veratraldehyde in presence of ammonia yields: (1) the *ammonium* derivative of γ-*dimethoxyphenyl* $\beta\beta'$-*dicyanoglutaconimide* [3 : 5-*dicyano*-2 : 6-*diketo*-4-m-p-*dimethoxyphenyldihydropyridine*],

$$C_6H_3(OMe)_2\cdot C{<}{\begin{matrix}C(CN)\text{---}CO\\CH(CN)\cdot CO\end{matrix}}{>}N\cdot NH_4,$$

which crystallises (with $2\frac{1}{2}H_2O$) from 70 per cent. alcohol in shining, white prisms; it begins to turn brown at 280—290°, but does not melt even at 300°. It is slightly soluble in alcohol, and its aqueous solution has an acid reaction to litmus. (2) *Ethyl* 3 : 4-*dimethoxyphenyl-α-cyanoacrylate*, $C_6H_3(OMe)_2\cdot CH\dot{:}C(CN)\cdot CO_2Et$, which crystallises from 90 per cent. alcohol in long, white needles showing blue fluorescence and melting at 156°; it is readily soluble in alcohol, acetone, benzene, and chloroform, and has the normal molecular weight in boiling acetone. (3) 3 : 4-*Dimethoxybenzylcyanoacetamide*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2,$$

crystallises from water in very slender needles, forming an almost gelatinous mass and melting at 173°; it is readily soluble in alcohol, and on being powdered becomes markedly electrified. T. H. P.

Combination of Mixed Organo-magnesium Compounds with the Pyridine and Quinoline Bases. Bernardo Oddo (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 100—106).—While primary and secondary amines react with mixed organo-magnesium compounds yielding hydrocarbons (for instance, magnesium ethyl iodide gives ethane), tertiary bases such as dimethylaniline do not react with these mixed compounds (Meunier, Abstr., 1903, i, 544). The author finds that the pyridine and quinoline bases react with organo-magnesium compounds yielding theoretical amounts of additive compounds, usually of the formula $(R)_2,I\cdot Mg\cdot ROEt_2$, where R represents the base. These substances, which may be employed to purify Grignard's compounds (Abstr., 1901, i, 263), exhibit the behaviour typical of the organo-magnesium derivatives.

The action of pyridine on magnesium methyl iodide in ethereal solution yields the unstable *compound*, $(C_5H_5N)_2,MgMe\cdot I,OEt_2,$

which is slightly soluble in ether, from which it is deposited as a fine powder; it reacts immediately with water, yielding methane; with benzaldehyde, it yields phenylmethylcarbinol, styrene, and polymerides of the last-named hydrocarbon. With magnesium phenyl bromide in ethereal solution, pyridine gives the *compound*,

$$(C_5H_5N)_2,MgPhBr,OEt_2,$$

which undergoes change in the air, is very slightly soluble in ether, and reacts with water, yielding benzene.

Quinoline and magnesium methyl iodide in ethereal solution yield the *compound*, $(C_9H_7N)_2,MgMeI,OEt_2$, which readily alters in the air. With magnesium phenyl bromide in ether, quinoline gives the *compound*, $(C_9H_7N)_2,MgPhBr$. T. H. P.

Potassium and Sodium Salt of Pyridine-3-sulphonic Acid. ERNST MURMANN (*Chem. Centr.*, 1904, ii, 454; from *Oesterr. Chem. Zeit.*, 7, 272—273).—Potassium pyridine-3-sulphonate,

$$C_5NH_4{\cdot}SO_3K,$$

crystallises from a hot aqueous solution in pointed needles, and the sodium salt, $C_5NH_4{\cdot}SO_3Na,1\frac{1}{2}H_2O$, in large, rectangular plates. Both salts are slightly yellow and readily soluble in water; the latter loses its water of crystallisation completely at 130°. E. W. W.

***iso*Pyrophthalone.** ALEXANDER EIBNER and K. HOFMANN (*Ber.*, 1904, 37, 3023—3026. Compare Abstr., 1903, i, 644).—Von Huber's *iso*pyrophthalone (Abstr., 1903, i, 576) is identical with Jacobsen and Reimer's pyrophthalone (Abstr., 1884, 335), which melts at 283°. G. Y.

Dinitrophenylpyridinium Chloride and its Products of Change. THEODOR ZINCKE, G. HEUSER, and W. MÖLLER (*Annalen*, 1904, 333, 296—345. Compare this vol., i, 448).—2 : 4-*Dinitrophenylpyridinium chloride*, $C_6H_3(NO_2)_2{\cdot}C_5NH_5Cl$, is prepared by heating a mixture of 1-chloro-2 : 4-dinitrobenzene with excess of pyridine on the water-bath; when solution is complete, the reaction sets in with development of heat; the salt crystallises in colourless needles, which decompose into its constituents at 200°. The same decomposition takes place when the salt is heated with dilute hydrochloric acid under pressure at 180—185°, but when heated with water at 150—160° dinitrophenol and pyridine are formed. The *platinichloride*, $[C_6H_3(NO_2)_2{\cdot}C_5NH_5]_2PtCl_6$, crystallises in yellow needles melting and decomposing at 221°. The corresponding *bromide* is prepared from 1-bromo-2 : 4-dinitrobenzene and pyridine, and forms pale yellow needles melting and decomposing into its constituents at 225°. The *perbromide*, $C_6H_3(NO_2)_2{\cdot}C_5NH_5{\cdot}Br_3$, is obtained by the action of bromine water on either the chloride or bromide, and crystallises in orange-yellow needles melting at 162—163°. The *periodide* crystallises in dark violet, lustrous needles melting at 125°. The *dichromate*, $[C_6H_3(NO_2)_2{\cdot}C_5NH_5]_2Cr_2O_7$, prepared from the chloride and aqueous potassium dichromate, crystallises in orange-yellow prisms melting and decomposing at 114—115°. In the foregoing decomposition of the

chloride by water, in addition to the formation of dinitrophenol and pyridine, *dinitrophenylpyridinium dinitrophenoxide*,

$$C_6H_3(NO_2)_2\cdot C_5NH_5\cdot O\cdot C_6H_2(NO_2)_2,$$

is also produced by union of the unchanged pyridinium base with the phenol; it crystallises in yellow needles melting at 142—143°.

Under the influence of alkali hydroxides or ammonia, the pyridinium chloride is converted into a *red* compound, which is probably represented by one of the formulæ: $C_6H_3(NO_2)_2\cdot N\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot OH$ or $C_6H_3(NO_2)_2\cdot NH\cdot CH\colon CH\cdot CH\colon CH\cdot CHO$; this compound is prepared most readily by treatment of the pyridinium compound with aqueous sodium carbonate until the original dirty-brown precipitate has become dark red and crystalline; from acetone, it forms deep red, rhombic crystals, which melt and decompose with elimination of pyridine at 180°, and is dissolved by alkalis with a dark violet coloration, slowly disappearing as the substance decomposes. When treated with hydrogen chloride in the absence of water, the original pyridinium salt is regenerated, but aqueous hydrogen chloride converts it into dinitroaniline; primary and secondary bases effect also the latter decomposition, but phenylhydrazine causes the elimination of water.

Attempts to convert the pyridine residue into some stable substance by oxidation failed; chromic acid in acetic acid solution leads to the formation of dinitroaniline and carbon dioxide; alkaline permanganate behaves in a similar manner, and nitric acid acts with extreme violence.

Attempts to prepare a methiodide were unsuccessful; when heated with methyl iodide and methyl alcohol at 100°, only dinitroaniline was produced. When boiled with alcohol, the ethyl ether of dinitrophenol and pyridine are formed, together with a small quantity of a substance crystallising in brownish-red leaflets, which dissolves in acetic acid with a deep red coloration.

The action of halogens on the red substance was tried in the hope of obtaining stable and characteristic additive products of the group $C_5H_6O_2$; additive compounds were formed, but they could not be isolated.

Primary aromatic amines react with dinitrophenylpyridinium chloride according to the equation: $C_6H_3(NO_2)_2\cdot C_5NH_5Cl + 2NH_2Ar = C_6H_3(NO_2)_2\cdot NH_2 + C_5H_7N_2Ar_2Cl$. The compound, which is produced together with the dinitroaniline, is the *hydrochloride* of a mono-acid base; it is intensely coloured and can be converted into the base. These compounds can be obtained from the red product, formed from the pyridinium chloride by the action of alkali, by treatment with the aromatic amine and subsequent addition of hydrogen chloride. Although certain substituted anilines can bring about this decomposition, 2 : 4-dichloroaniline and the three nitroanilines are unable to do so. These compounds appear to have the constitution

$$NAr\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot NHAr,HCl,$$

and have the character of dyes, most being coloured intensely red, but some existing also in a bluish-violet modification. The red form is obtained from dilute alcohol, whilst the violet form is obtained on drying or on crystallising from absolute alcohol or acetone. In some cases, these two forms are dimorphous, but in others are due to the presence of water or alcohol of crystallisation.

The *hydrochloride* of the dianilide, NPh:CH·CH:CH·CH:CH·NHPh, is prepared from aniline and the pyridinium chloride, and crystallises in dark red needles melting at 143—144°; the *platinichloride*,

$$(C_{17}H_{17}N_2)_2PtCl_6,$$

is a reddish-brown, crystalline powder melting and decomposing at 179—180°. The *hydrobromide* forms red, lustrous needles, becoming violet on drying and melting at 167°. The *base* crystallises in yellow leaflets or brownish-red needles, which decompose slowly on keeping and melt and decompose at 85—86°.

The *hydrochloride* of di-*p*-chlorodianilide, $C_{17}H_{14}N_2Cl_2$,HCl, crystallises in reddish- or bluish-violet needles melting and decomposing at 143°; the free *base* crystallises in yellow or reddish-brown needles or in hydrated, yellow needles melting and decomposing at 108—110°, and, although it decomposes on keeping, is more stable than the unsubstituted base. When heated with acetic anhydride, *p*-chloroacetanilide and an *acetyl* derivative, C_6H_4Cl·N:CH·CH:CH·CH:CH·OAc, which crystallises in colourless needles or plates melting at 129°, are produced.

The *hydrochloride* of the di-*m*-chlorodianilide, $C_{17}H_{14}N_2Cl_2$,HCl, crystallises in steel-blue or red needles melting and decomposing at 135—136°; the free *base* forms yellow, lustrous leaflets or reddish-brown needles melting at 109°.

The *hydrochloride* of the di-*p*-toluidide, $C_{17}H_{14}N_2Me_2$,HCl, prepared as the compounds just described, crystallises in slender, red needles or in dark red, rhombic plates, or in forms which are bluish-violet by reflected light and garnet-red by transmitted light; it melts at 142—143°. The free *base* crystallises in golden plates or red needles melting and decomposing at 121°. The *hydrochloride* of the di-*o*-toluidide is more soluble than that of the para-compound, and crystallises in leaflets or plates melting and decomposing at 148°. The free *base* is oily and unstable.

The *hydrochloride* of the di-*as*-xylidide, $C_{17}H_{12}N_2Me_4$,HCl, crystallises in pale red leaflets melting and decomposing at 145°; the free *base* is an oil. The *hydrochloride* of the di-ψ-cumidide, $C_{17}H_{10}N_2Me_6$,HCl, crystallises in dark red or violet needles melting and decomposing at 134° or in lustrous, red plates melting at 144—145°. The free *base* crystallises in golden leaflets or red needles melting and decomposing at 93°.

The action of phenylhydrazine on dinitrophenylpyridinium chloride is represented by the equation: $C_6H_3(NO_2)_2 \cdot C_5NH_5Cl + N_2H_3Ph = C_6H_3(NO_2)_2 \cdot C_5NH_5 \cdot N_2H_2Ph + HCl$; the pyridine ring is broken, as in the case of alkalis and aliphatic amines. The phenylhydrazine *compound*, which has either the formula

$$C_6H_3(NO_2)_2\text{·N:CH·CH:CH·CH:CH·NH·NHPh}$$

or the formula $C_6H_3(NO_2)_2$·NH·CH:CH·CH:CH·CH:N·NHPh, crystallises in black, lustrous needles melting and decomposing at 140°.

The dianilides under a variety of conditions can be converted into quaternary pyridinium bases, the pyridine ring being again regenerated: NAr:CH·CH:CH·CH:CH·NHAr,HCl = NH_2Ar + C_5NH_5ArCl. The reaction takes place very readily when the salt is heated with hydrochloric acid, or when the hydrochloride is melted, or by heating

the salt with arylamines. The method of preparation last mentioned permits of these bases being prepared directly from the dinitrophenylpyridinium chloride, which is for this purpose heated in alcoholic solution with excess of amine. The pyridinium base is separated from the amine by precipitating with mercuric chloride, which forms an insoluble compound with the former.

Phenylpyridinium chloride, C_5NH_5PhCl,H_2O, forms colourless, monoclinic crystals, which are hygroscopic in moist air and melt at 105—106°. The *picrate* crystallises in needles melting at 123—124°; the *platinichloride*, $(C_5NH_5PhCl)_2PtCl_4$, crystallises in orange-red needles melting and decomposing at 202—203°. The *dichromate* crystallises in dark yellow needles melting at 162—163° and decomposing at 180°.

p-*Chlorophenylpyridinium chloride*, $C_5NH_5Cl{\cdot}C_6H_4Cl$, crystallises in colourless prisms or needles melting at 123—124°; from the aqueous solutions of this salt, alkali hydroxides precipitate a brownish-red solid melting at 201—202°; the *picrate* crystallises in pale yellow needles melting at 143—144°; the *platinichloride* crystallises in orange-red needles melting and decomposing at 222—223°, and the *dichromate* in orange, six-sided leaflets melting at 192—193° and then exploding.

o-*Chlorophenylpyridinium chloride*, $C_5NH_5Cl{\cdot}C_6H_4Cl,H_2O$, prepared by heating the dinitro-compound with *o*-chloroaniline on the water-bath, crystallises in concentric groups of needles or leaflets melting at 88—93°; the *picrate* crystallises in yellow needles melting at 104—105°, the *platinichloride* in orange-red needles melting at 204—205°, and the *dichromate* in yellow needles melting and decomposing at 111°.

The dianilides are decomposed by bromine; thus, the compound from aniline and the dinitro-compound yields *s*-tribromoaniline (m. p. 118°) and s-*tribromophenylpyridinium perbromide*, $C_5NH_5Br{\cdot}C_6H_2Br_3,Br_2$, which crystallises in yellow leaflets melting and decomposing at 212—214°. When the latter is warmed with acetone, s-*tribromophenylpyridinium bromide* is formed, crystallising in white needles melting and decomposing at 310—312°; the *dichromate* forms yellow crystals melting and decomposing at 160°.

The *p*-chlorodianilide behaves in a similar manner; 2 : 6-dibromo-4-chloroaniline (m. p. 95°) and the *perbromide* of 2 : 6-dibromo-4-chlorophenylpyridinium bromide, $C_5NH_5Br{\cdot}C_6H_2ClBr_2,Br_2$, are formed; the latter, which crystallises in golden-yellow leaflets melting and decomposing at 217—219°, is converted by warming with acetone into the bromide, $C_5NH_5Br{\cdot}C_6H_2ClBr_2$, which crystallises in white needles melting and decomposing at 270—271° and is reconverted into the perbromide by treatment with bromine. The *platinichloride* melts and decomposes at 266—268°, and the *dichromate*, which forms yellow crystals, at 151°.

The author discusses the constitution of the dyes described in the foregoing, concludes that they are identical with the compounds obtained by König by the action of amines on bromocyanopyridine (this vol., i, 449), and agrees with König as to the constitution of these substances.

K. J. P. O.

Behaviour of Tertiary Amines towards Organo-magnesium Compounds. FRANZ SACHS and LUDWIG SACHS (*Ber.*, 1904, **37**, 3088—3092).—Quinoline combines with magnesium phenyl bromide dissolved in absolute ether to form a greyish-white additive *compound*, $C_9H_7N,MgPhBr$, which is sparingly soluble in ether; the nitrogen atom is here probably quinquevalent, as water readily decomposes the compound giving quinoline. That the substance does not contain magnesium phenyl bromide as such is shown by the fact that the latter cannot be detected by means of Michler's ketone. If the substance were formed by addition to a double linking of the nucleus, decomposition by water would give a dihydroquinoline and not quinoline as is actually the case.

The additive *compound*, $C_9H_7N,MgEtBr$, is less stable than the analogous phenyl derivative; it is decomposed by alcohol giving ethane. W. A. D.

A New So-called *L*-Reaction. LUDWIG PAUL (*Chem. Zeit.*, 1904, **28**, 702—703).—When an aniline salt is heated with glycerol at 215° for an hour, a *base*, "*AL*," which perhaps is a tetrahydroquinoline derivative, $C_6H_4<\begin{matrix}CH_2\cdot CH \\ NH\cdot CH\cdot C_6H_4\cdot NH_2\end{matrix}$, is obtained; it is easily diazotised and coupled with phenols. Similar compounds are obtained by heating glycerol with the hydrochlorides of sulphanilic acid, *α*-naphthylamine, *p*-phenylenediamine, *p*-aminoacetanilide, *p*-nitroaniline, and dimethylaniline. No analyses are given of any of the products. W. A. D.

Some New Dyes. LUDWIG PAUL (*Chem. Zeit.*, 1904, **28**, 703—704).—A detailed account of the interaction of glycerol with dimethylaniline and with *m*-phenylenediamine (compare preceding abstract). No analyses are given of the products nor are formulæ ascribed to them. W. A. D.

***β*-Ethylquinuclidine.** WILLIAM KOENIGS (*Ber.*, 1904, **37**, 3244—3252).—On heating methylolhexahydro-*β*-collidine, $OH\cdot C_9H_{18}N$, for some hours with fuming hydriodic acid and phosphorus, a compound, $C_9H_{18}NI,HI$, is formed, which when crystallised from alcohol is colourless, melts and decomposes at 233°, and on cautious treatment with sodium hydroxide is converted into 3-*ethylquinuclidine*,

$$N\begin{matrix}\diagup CH_2-CH_2 \diagdown \\ -CH_2-CH_2- \\ \diagdown CH_2\cdot CHEt \diagup\end{matrix}CH.$$

This is a colourless oil with an odour similar to collidine, boiling at 190—192° under 720 mm. pressure, has a molecular weight of 139° and forms a series of well-defined salts. The *picrate* crystallises in bright yellow flat needles melting at 153—154·5°; the *hydrochloride* is colourless and melts at 208—211°; the *aurichloride* forms golden, glistening plates, which melt at 176—178°; the *platinichloride* melts and decomposes at 221°, and the *mercurichloride* crystallises in colourless prisms easily soluble in water. 3-Ethylquinuclidine does not react with per-

manganate or naphthalenesulphonic chloride. The *methiodide* crystallises from chloroform in colourless plates melting at 55—80°, but possibly still contains some of the solvent; the *methochloride*, which is very hygroscopic, forms a sparingly soluble, reddish-yellow *platinichloride*, melting and decomposing at 265°, and also an *aurichloride* melting at 187°.

The ethyl cincholeuponate derived by Skraup from one of the cinchonine alkaloids gives on reduction with sodium and alcohol a base forming a crystalline *aurichloride*, $C_9H_{19}ON,HAuCl_4$, which melts at 90—99°. This base, when heated with hydriodic acid and phosphorus, forms a compound $C_9H_{18}NI,HI$, melting at 138—139°, which, after a time, is converted into a base, $C_9H_{17}N$, of which the derivatives very closely resemble those of β-ethylquinuclidine; the hydriodide melts at 227—230°, the hydrochloride at 210—212°, the picrate at 153—155°, the platinichloride at 223° (under decomposition), and the aurichloride at 176—177°. A 0·5 gram solution of the hydrochloride in 6 c.c. of water shows an optical rotation $a_D + 5°$ in a 1 dcm. tube. The base thus appears to be an optically active form of β-ethylquinuclidine. E. F. A.

2-Phenylquinoline. ERNST MURMANN (*Chem. Centr.*, 1904, ii, 454; from *Oesterr. Chem. Zeit.*, 7, 273).—2-Phenylquinoline boils at 363° (corr.), melts at 84°, and solidifies at 80—81°; it is very sparingly soluble in cold light petroleum or alcohol, but somewhat more soluble in hot light petroleum, and readily so in hot alcohol, benzene, ethyl acetate, amyl acetate, ether, carbon disulphide, or acetone. The base shows strong triboluminescence; even small fragments emit light when shaken violently in the dark. E. W. W.

Action of Magnesium Benzyl Chloride on Cyclaminones. HERMANN DECKER and ROBERT PSCHORR [and, in part, O. KOCH and HANS EINBECK] (*Ber.*, 1904, 37, 3396—3404. Compare this vol., i, 344, 611).—The action of magnesium benzyl chloride on 10-methyl-9-acridone leads to the formation of 9-benzylidene-10-methyl-9 : 10-dihydroacridine (this vol., i, 620).

1-*Benzyl*iso*quinoline methiodide*, $C_{16}H_{13}N,MeI$, is obtained on addition of a concentrated aqueous solution of potassium iodide to the solution in dilute sulphuric acid of the product from the action of magnesium benzyl chloride on 2-methyl*iso*quinolone. It crystallises in flat, yellow needles, commences to sinter at 230°, and melts and decomposes at 247—248°. With potassium hydroxide in concentrated aqueous solution, it yields a precipitate of 1-*benzylidene*-2-*methyl*-1 : 2-*dihydro*iso*quinoline*, the parent substance of the *iso*papaverine bases; this dissolves in benzene or ether to a yellow solution, and forms the colourless ammonium base with water. When heated for some time over its melting point, the methiodide loses methyl iodide and yields 1-benzyl*iso*quinoline, which, when almost pure, boils at 211—213° under 11 mm. pressure (Rügheimer, Abstr., 1900, i, 522); the *hydrochloride* crystallises in glistening needles and melts at 171—172°; the *picrate* crystallises in prisms and melts and decomposes at 184—185° (corr.); the *platinichloride* melts and decomposes at 218°. 2-*Benzylquinoline methiodide*, obtained by the action of potassium iodide on the

product from the interaction of magnesium benzyl chloride and 1-methylquinolone, crystallises in long, yellow needles, decomposes when heated above 220°, and, when acted on by an alkali hydroxide yields the yellow *benzylidene* base, which does not form an ammonium base with water. In the same manner, 6 : 7-*dimethoxy*-1-*benzyl*iso*quinoline methiodide* is prepared from magnesium benzyl chloride and 6 : 7-dimethoxy-2-methyl*iso*quinolone. It crystallises in thick, yellow prisms, melts at 206—207°, and gives the *iso*papaverine reactions.

N-Methyl*iso*papaverine (this vol., i, 338) or *N*-methylpapavarinium methyl sulphate was oxidised in alkaline aqueous solution by the passage of a current of air during 8 days. After extraction with benzene, the distillation residue was dissolved in hot hydrochloric acid, and, on cooling, dimethoxy-2-methyl*iso*quinoline hydrochloride, $C_{12}H_{13}O_3N,HCl,2H_2O$, crystallised out on cooling. It forms colourless needles and melts at 160—175°. The free *base*, $C_{12}H_{13}O_3N$, melts at 109—110° (Pschorr, this vol., i, 611). The sparingly soluble *hydriodide* rapidly becomes brown on exposure to air; the yellow, crystalline *picrate* melts at 136—137°. *Dimethoxy*-2-*ethyl*iso*quinolone hydrochloride*, obtained in the manner as the 2-methyl salt, contains $2H_2O$ and melts and decomposes at 142—150°; the *base* melts at 60—62°.

The methyl ether of vanillin (veratraldehyde), which melts at 42—43°, is obtained as a product of the oxidation of *N*-methyl*iso*papaverine (compare this vol., i, 339). Veratric acid and probably veratryl alcohol are also formed by the prolonged action of the alkali hydroxide. The oxidation of the *iso*papaverinium bases can be carried out also with potassium ferricyanide or permanganate.

Veratryl alcohol, $OH\cdot CH_2\cdot C_6H_3(OMe)_2$ [1 : 3 : 4], formed along with veratric acid by the action of warm concentrated sodium hydroxide solution on veratraldehyde, is a viscid, colourless oil which boils at 172—173° under 14 mm., or at 296—297° under 732 mm. pressure, and gives a red coloration with concentrated sulphuric acid. *Veratryl chloride*, $CH_2Cl\cdot C_6H_3(OMe)_2$, formed by the action of hydrogen chloride on the alcohol in benzene solution, crystallises in colourless needles and melts at 50—51°. The *chloride* and the *bromide*, obtained in the same manner, yield the alcohol when treated with cold water. G. Y.

Preparation of Acridinium Dyes. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 152662).—On heating acridinium compounds or their leuco-compounds with concentrated sulphuric acid and 2 or 3 mols. of formaldehyde in open vessels, orange-red dyes are obtained, consisting partly of acridine compounds, but chiefly of acridinium derivatives. The two classes may be separated by means of ammonia. The products are not identical with those obtained by heating acridine-yellow, &c., with formaldehyde and dilute hydrochloric acid under pressure (D.R.-P. 135771). C. H. D.

Researches in the Phenylacridine Group. EDMOND LANDAUER (*Bull. Soc. chim.*, 1904, [iii], 31, 1083—1094. Compare Bernthsen, Abstr., 1883, 580, 1099, 1133, and 1884, 1356, 1357; and Hess and Bernthsen, Abstr., 1885, 800).—5-o-*Hydroxyphenylacridine*,

$$C_6H_4<\begin{matrix}C(C_6H_4\cdot OH)\\ |\\ N\text{———————}\end{matrix}>C_6H_4,$$

is best prepared by mixing diphenylamine (1 mol.) with dry salicylic acid (1·5 mols.) and zinc chloride (3 mols.) and heating for five hours at 170—175°, the mixture being well stirred throughout the operation. When cold, the mass is extracted with alcohol and the solution poured into excess of water; the precipitate is washed successively with water, ammonia solution, and light petroleum, and finally recrystallised from alcohol. The substance crystallises in greenish-yellow, microscopic prisms and melts and decomposes at 289—290° (corr.). It is soluble in solutions of the alkali hydroxides and in acids (the solution in sulphuric acid is fluorescent), but is only slightly soluble in organic liquids and insoluble in water.

5-*Di*-m-*phenylacridinyl ether*, prepared from diphenylamine and *m*-hydroxybenzoic acid, separates from boiling aniline in yellow, monoclinic crystals and may be purified by sublimation at 325° under 20 mm. pressure and then melts and decomposes at 366—367°. Ebullioscopic determinations of the molecular weight give anomalous results. It is readily soluble in aniline, nitrobenzene, and quinoline, but is insoluble or nearly so in most other organic solvents and water. The solution in sulphuric acid fluoresces green. The *salts* are sparingly soluble in water and acids; the *platinichloride* forms fine, reddish-yellow, monoclinic crystals, and the *aurichloride*, golden-yellow crystals; the *picrate*, fine yellow needles or elongated prisms, and melts at 245°. When the ether is heated with ethyl iodide in closed tubes at 180° to 185° for seven hours, the *diethiodide* is obtained; this forms brownish-black crystals, is soluble in alcohol, melts at 208—209°, and is converted by warming with a solution of potassium hydroxide into a yellow *substance*, which melts and decomposes at 359—360°. With acetic anhydride, the *acetate* of the ether is produced.

5-p-*Hydroxyphenylacridine*, prepared by the method already described, using *p*-hydroxybenzoic acid, forms yellow, monoclinic crystals, and melts and decomposes at 355—356°. It is soluble in aniline, naphthalene, boiling diphenylamine, and in alkalis, less so in alcohols, and insoluble in water. The solution in sulphuric acid fluoresces strongly green, that in hydrochloric acid is similarly, but less vividly, fluorescent. The *dichromate* forms yellowish-red needles, the *picrate*, slender, yellow needles, the *platinichloride*, reddish-yellow crystals, and the *aurichloride*, yellow, monoclinic crystals. *Sodium* 5-p-*hydroxyphenylacridinesulphonate*, prepared in the usual manner, forms crystalline scales with a pink tint; it is readily soluble in the usual solvents.

Solutions of these three compounds in acetic acid possess no tinctorial power, whereas the solutions in mineral acids dye wool, cotton, silk, and leather in yellow tints. Since the introduction of the hydroxyl group into the 5-phenyl nucleus of phenylacridine gives rise to dyes, it appears likely that the amino-group would behave similarly, although Hess and Bernthsen (*loc. cit.*) state that 5-*p*-aminophenylacridine has no tinctorial power. T. A. H.

Transformation of *o*-Nitro- and *o-p* Dinitrobenzyl Chlorides into Acridine Derivatives. CARLO BAEZNER (*Ber.*, 1904, 37, 3077—3083).—Instead of using *o*-aminobenzyl alcohol in the synthesis

of 1 : 2-phenonaphthacridine from β-naphthol (Ullmann and Baezner, Abstr., 1902, i, 694), the author heats *o*-nitrobenzyl chloride with stannous chloride, β-naphthol, and hydrochloric acid in alcoholic solution. 1 : 2-*Phenonaphthacridine nitrate* forms yellow crystals melting at 217°, and the *hydrochloride* crystallises from alcohol. β-Naphthylamine or phenyl-β-naphthylamine can be substituted for β-naphthol in the condensation.

5-*Hydroxy*-1 : 2-*phenonaphthacridine*, $C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{N}{>}C_{10}H_5\cdot OH$, prepared similarly from 2 : 7-dihydroxynaphthalene and *o*-nitrobenzyl alcohol or *o*-nitrobenzyl chloride, crystallises from nitrobenzene in yellowish-brown needles having a bronze-like lustre and melts at 322°; the *hydrochloride* forms red crystals and the *methochloride* crystallises from alcohol in red needles.

9-*Amino*-1 : 2-*phenonaphthacridine*, $NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{CH}{N}{>}C_{10}H_6$, prepared from 2 : 4-dinitrobenzyl chloride and β-naphthol, crystallises from toluene or dilute alcohol in yellow needles and melts at 270°. The *hydrochloride* forms red crystals and the *picrate* yellowish-red needles.
W. A. D.

A New Formation of Naphthacridines. [Phenonaphthacridines]. FRITZ ULLMANN and ANTONIO LA TORRE (*Ber.*, 1904, **37**, 2922—2928. Compare Abstr., 1902, i, 119).—*o*-Tolyl-α-naphthylamine (Friedländer, Abstr., 1884, 79) is best prepared by fusing α-naphthol with *o*-toluidine hydrochloride. Lead oxide converts it into 2 : 1-phenonaphthacridine, $\begin{array}{l} CH\cdot CH{:}C\cdot CH\cdot C{:}CH\cdot CH{:}C\cdot CH{:}CH \\ CH\cdot CH{:}C\cdot N - C{=\!=\!=\!=}C\cdot CH{:}CH \end{array}$, crystallising from benzene and light petroleum in long, glistening needles and melting at 108°. The picrate separates from nitrobenzene in small, yellow crystals and melts and decomposes at 226—229°. The hydrochloride forms yellow needles and sinters at 241°, and melts and decomposes at 244°. The alcoholic solution is yellow with bluish-green fluorescence. The nitrate forms yellow leaflets and melts and decomposes at 188—189°. The *methiodide*, $C_{18}H_{14}NI$, prepared by warming the base with methyl sulphate, and precipitating the aqueous solution with potassium iodide, crystallises from alcohol in orange needles, melts at 262—263°, and dissolves in hot alcohol to a yellow solution with bluish-green fluorescence. Alkali hydroxides precipitate the yellow, crystalline carbinol-base from the aqueous solution.

2 : 1-Phenonaphthacridine is identical with Pictet and Erlich's α-chrysidine (Abstr., 1891, 216).

1 : 2-Phenonaphthacridine, prepared by heating *o*-tolyl-β-naphthylamine with sulphur or lead oxide, melts at 131° and is identical with the product from *o*-aminobenzyl alcohol (Ullmann and Baezner, Abstr., 1902, i, 694) and with Pictet and Erlich's β-chrysidine. The picrate forms needles and sinters at 255°, and melts and decomposes at 260°. The hydrochloride forms long, yellow needles; the nitrate forms yellow needles, and melts and decomposes at 217°. The methiodide forms orange, felted needles, becoming orange-red on heating and melting

at 264°, and dissolves sparingly in hot water to a yellow solution with slight green fluorescence.

The melting points found are considerably higher than those obtained by Pictet and Erlich.

12-*Methyl*-1 : 2-*phenonaphthacridol*, $C_{18}H_{15}ON$, prepared by addition of ammonia to a solution of the methiodide, separates from benzene in small, slightly pink, glistening crystals, becoming red at 160°, brown at 190°, sintering at 195°, and melting at 206—207°. The solutions in alcohol, ether, or toluene are colourless, with blue fluorescence, that in acetic acid is yellow with bluish-green fluorescence.

C. H. D.

Constitution of Quinophthalone. Alkali Derivatives of Quinophthalone and of *iso*Quinophthalone. ALEXANDER EIBNER and H. MERKEL (*Ber.*, 1904, **37**, 3006—3011. Compare Abstr., 1901, i, 348; 1902, i, 494, 644).—When dissolved in absolute ethyl alcohol and treated with sodium ethoxide, quinophthalone yields the sodium derivative, $C_{18}H_{10}O_2NNa$, which is obtained as a scarlet powder, consisting of sheaves of microscopic needles. This sodium derivative is obtained also by the action of sodium hydroxide on quinophthalone in benzene or chloroform solution, or, with evolution of hydrogen, by the action of sodium on quinophthalone in dry benzene or xylene solution, or by treatment of *iso*quinophthalone (Abstr., 1902, i, 644) with sodium ethoxide in absolute alcoholic solution. The potassium derivative, $C_{18}H_{10}O_2NK$, obtained by the action of potassium ethoxide on quinophthalone, forms orange-coloured, microscopic, slender needles. These alkali derivatives yield quinophthalone when treated with water, or when repeatedly washed with 96 per cent. alcohol. They have probably the constitution $C_6H_4<\begin{matrix}CO\\C(OM)\end{matrix}>C\cdot C_9H_6N$ (compare Gabriel, Abstr., 1893, i, 415).

G. Y.

***iso*Quinophthalone.** ALEXANDER EIBNER and K. HOFMANN (*Ber.*, 1904, **37**, 3011—3018. Compare Abstr., 1902, i, 644).—When boiled with aqueous alkali hydroxides, *iso*quinophthalone slowly dissolves to a yellow solution, which, on addition of acetic acid, yields a yellow, flocculent precipitate. The product, *quinolylacetophenone*-o-*carboxylic acid*, $C_9H_6N\cdot CH_2\cdot CO\cdot C_6H_4\cdot CO_2H$, separates from its solution in acetone, on addition of water, in yellow, prismatic crystals, melts and decomposes at 155°, is easily soluble in chloroform, benzene, or acetone, and in aqueous alkali hydroxides or carbonates, or mineral acids. The aqueous solutions of the *alkali* salts give precipitates with the salts of the heavy metals. The *oxime*, $C_{18}H_{13}O_2N{:}NOH$, crystallises in matted needles, melts and decomposes at 145°, is easily soluble in aqueous alkali hydroxides, and yields ammonia and quinaldine when heated with soda-lime. With phenylhydrazine, the acid yields a *phthalazone*, $C_9H_6N\cdot CH_2\cdot C\Big<\begin{matrix}C_6H_4\cdot CO\\ \vert \qquad \vert \\ N \text{——} NPh\end{matrix}$, which crystallises in white, matted needles, melts at 102—105°, yields fluorescein when heated with resorcinol and zinc chloride, and evolves quinaldine when heated with soda-lime. When acted on by sodium nitrite and dilute hydrochloric

acid, the acid yields an iso*nitroso*-derivative, $C_{18}H_{12}O_4N_2$, which crystallises in colourless, slender needles, and melts and decomposes, with formation of quinophthalone, at 205°. The action of benzenediazonium chloride on the acid, dissolved in aqueous sodium hydroxide, leads to the formation of a red precipitate of *quinolylformazyl*, $NHPh\cdot N:C(C_9NH_6)\cdot N:NPh$, which crystallises in reddish-brown needles, melts and decomposes at 185°, and dissolves in hot dilute hydrochloric acid to a red, in concentrated sulphuric to a blue, solution, which changes to orange-red on dilution. It yields quinaldine when heated with soda-lime, aniline, phenylhydrazine, and quinaldine when reduced with zinc and hydrochloric acid.

Quinolylacetophenone-*o*-carboxylic acid is converted into quinophthalone when heated above its melting point, or when warmed with concentrated sulphuric acid, the product being precipitated on addition of water, and when heated with benzaldehyde.

The following homologues of *iso*quinophthalone have been obtained by heating the corresponding quinaldine with phthalic anhydride. 8-*Methyl*iso*quinophthalone*, from 2 : 8-dimethylquinoline, crystallises in yellow needles and melts at 235°; 6-*methyl*iso*quinophthalone*, from 2 : 6-dimethylquinoline, crystallises in yellow needles and melts at 237°; 6 : 8-*dimethyl*iso*quinophthalone*, from 2 : 6 : 8-trimethylquinoline, crystallises in yellow needles and melts at 231°; 5 : 6 : 8-*trimethyl*iso*quinophthalone*, from 2 : 5 : 6 : 8-tetramethylquinoline, forms yellow needles and melts at 236°; *β-naphtha*iso*quinophthalone*, from *β*-naphthol-2-methylquinoline, crystallises in yellow needles and melts at 273°. These *iso*quinophthalones are less highly coloured, and usually melt at a lower temperature than the corresponding quinophthalones, into which they are converted by means of sodium ethoxide. They give the characteristic red formazyl derivative with benzenediazonium chloride and alkali. G. Y.

Quinophthalone, *iso*Quinophthalone, and Quinophthaline. ALEXANDER EIBNER and K. HOFMANN (*Ber.*, 1904, **37**, 3018—3023. Compare Abstr., 1901, i, 348).—When heated with excess of phenylhydrazine, quinophthaloneanil is converted into *quinophthalonephenylhydrazone*, $C_{18}H_{11}ON:N_2HPh$, which crystallises in dark red needles and thin plates, melts at 206°, gives Bülow's reaction, and is hydrolysed by concentrated hydrochloric acid at 210°, with formation of quinophthalone and *p*-phenylenediamine.

With bromine in chloroform solution, *iso*quinophthalone forms a scarlet, crystalline *perbromide*, which is converted by sulphurous acid into a yellow bromine compound, by ammonia into *iso*quinophthalone. The filtrate from the perbromide deposits salmon-coloured needles which are a mixture of the perbromide and the monobromo-compound (compare Abstr., 1902, i, 644). With a limited quantity of bromine, *iso*quinophthalone yields a *monobromo*-derivative, $C_{18}H_{10}O_2NBr$, which crystallises in yellow needles, commences to lose bromine at 170°, melts at 275°, and yields *iso*quinophthalone when treated with dilute ammonia.

The action of bromine on *β*-quinophthaline in chloroform solution leads to the formation of a dark red *perbromide*, which loses the whole

of its bromine on treatment with sulphurous acid or ammonia, and a *tetrabromo*-derivative, which crystallises in colourless prisms, melts at 78°, and must have the constitution $C_9H_6N\cdot CBr_2\cdot CBr<{C_6H_4 \atop NBr}>CO$. When boiled with sodium hydroxide solution, tetrabromo-β-quinophthaline dissolves to a golden-yellow solution, which gives the quinolylacetophenonecarboxylic acid reaction with benzenediazonium chloride.

In future, quinophthalone and α-quinophthaline are to be termed *s*-quinophthalone and *s*-quinophthaline; the *iso* series will be termed *as*-quinophthalone and *as*-quinophthaline. G. Y.

Derivatives of Diacetonalkamines. II. MORITZ KOHN (*Monatsh.*, 1904, 25, 817—849. Compare this vol., i, 378).—The action of formaldehyde on diacetonalkamine [methyl-β-amino*iso*butylcarbinol] leads to the formation of 4 : 4 : 6 *trimethyltetrahydro*-1 : 3-*oxazine*, $O<{CH_2—NH \atop CHMe\cdot CH_2}>CMe_2$, which is a mobile liquid with an intense basic odour, boils at 149—152°, is easily soluble in ether, and absorbs moisture and carbon dioxide. The *hydrochloride* is a viscid syrup; the *aurichloride*, $C_7H_{15}ON,HAuCl_4$, melts at 140—143°; the *platinichloride* forms glistening needles; the crystalline *picrate*, $C_7H_{15}ON,C_6H_3O_7N_3$, melts at 118° or at 131° after sintering at 124°, depending on the manner of heating. The *nitroso*-derivative,

$$C_7H_{14}O_2N_2,$$

is a mobile liquid with an aromatic odour and boils at 129—131° under 22—24 mm. pressure. The *acetyl* derivative, $C_7H_{14}ONAc$, is a colourless liquid, boils at 123—125° under 19 mm. and at 235—237° under atmospheric pressure; its *aurichloride*, $C_9H_{17}O_2N,HAuCl_4$, is crystalline. The action of methyl iodide on the base in methyl alcoholic solution leads to the formation of the *methiodide* of the methylated base, which, with silver chloride, yields the *methochloride* as a syrup, crystallising after some weeks; the *aurichloride*, $C_9H_{19}ON,HAuCl_4$, melts and decomposes at 241°; the *platinichloride*,

$$(C_9H_{19}ON)_2,H_2PtCl_6,$$

forms a yellowish-red, crystalline precipitate and melts and decomposes at 255°.

3 : 4 : 4 : 6-*Tetramethyltetrahydro*-1 : 3-*oxazine*,

$$O<{CH_2—NMe \atop CHMe\cdot CH_2}>CMe_2,$$

boils at 166—168° and mixes with water with development of heat; the *hydrochloride* is a colourless syrup; the *platinichloride*,

$$(C_8H_{17}ON)_2,H_2PtCl_6,$$

forms a sandy, glistening, crystalline powder; the *aurichloride*, $C_8H_{17}ON,HAuCl_4$, crystallises in glistening leaflets, commences to soften at 80°, melts almost completely at 120°, and is liquid at 136°; the *picrate* crystallises in slender needles and melts at 171—173°. With methyl iodide, the base yields the same methiodide as is obtained from the secondary base. With ethyl iodide, the tertiary base forms the *ethiodide;* when treated successively with silver and gold chlorides, it yields the *aurichloride*, $C_{10}H_{21}ON,HAuCl_4$, which crystallises in

slender needles, commences to decompose at 175°, and melts at 204°; the *platinichloride*, $(C_{10}H_{21}ON)_2,H_2PtCl_6$, forms an orange-yellow, crystalline precipitate and melts at 230°.

Ethyldiacetonalkamine [*methyl-β-ethylamino*iso*butylcarbinol*],

$$NHEt\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OH,$$

obtained by reduction of ethyldiacetonamine, prepared from mesityl oxide and ethylamine, is a colourless liquid with an ammoniacal odour, boiling at 189—191°; the orange-coloured *platinichloride*,

$$(C_8H_{19}ON)_2,H_2PtCl_6,$$

is sparingly soluble in water. 3-*Ethyl*-4 : 4 : 6-*trimethyltetrahydro*-1 : 3-*oxazine*, $O<\begin{matrix}CH_2\text{---}NEt\\CHMe\cdot CH_2\end{matrix}>CMe_2$, formed by the action of formaldehyde on ethyldiacetonalkamine, boils at 176—180°; the *hydrochloride* is a viscid, colourless syrup; the *aurichloride*, $C_9H_{19}ON,HAuCl_4$, crystallises in long needles and melts at 180—182°; the *platinichloride* crystallises in glistening prisms; the crystalline picrate melts at 112—115°. With methyl iodide, the base yields the same quaternary iodide as is obtained by the action of ethyl iodide on the tetramethyl base.

The action of methyl iodide on β-amino*iso*hexylcarbinol leads to the formation of a quaternary *iodide*, which, on successive treatment with silver and gold chlorides, yields the *aurichloride*,

$$OH\cdot CMe_2\cdot CH_2\cdot CHMe\cdot NMe_3AuCl_4,$$

which crystallises in glistening needles and melts at 106—108°; the *platinichloride*, $(C_9H_{22}ON)_2PtCl_6$, crystallises in leaflets and melts at 105°. G. Y.

Derivatives of Diacetonalkamines. III. MORITZ KOHN (*Monatsh.*, 1904, 25, 850—864).—4:4:6-*Trimethyl*-2-iso*propyltetrahydro*-1 : 3-*oxazine*, $O<\begin{matrix}CHPr^{\alpha}\cdot NH\\CHMe\cdot CH_2\end{matrix}>CMe_2$, obtained by treating diacetonalkamine with *iso*butaldehyde, is a clear, mobile liquid and boils at 171—173° under 744 mm. pressure; the *aurichloride*,

$$C_{10}H_{21}ON,HAuCl_4,$$

crystallises in needles and melts and decomposes at 144°; the *platinichloride*, $(C_{10}H_{21}ON)_2,H_2PtCl_6$, crystallises from the concentrated solution. The *nitroso*-derivative, $C_{10}H_{20}O_2N_2$, is a yellow oil, which appears to decompose when distilled in a vacuum or in a current of steam.

3 : 4 : 4 : 6-*Tetramethyl*-2-iso*propyltetrahydro*-1 : 3-*oxazine*, obtained from methyldiacetonalkamine and *iso*butaldehyde, distils at 190—194° under 750 mm. pressure; the *aurichloride*, $C_{11}H_{23}ON,HAuCl_4$, crystallises in long, thin needles and melts and decomposes at 140°; the *platinichloride* crystallises in plates and leaflets. With methyl iodide, the base forms a *methiodide* which is converted by silver chloride into the *methochloride;* the *aurichloride*, $C_{11}H_{23}ONMeAuCl_4$, melts at 123—126°.

2-*Phenyl*-4 : 4 : 6-*trimethyltetrahydro*-1 : 3-*oxazine*, obtained from diacetonalkamine and benzaldehyde, is a viscid, colourless oil which boils at 131° under 10 mm. pressure; the *platinichloride*,

$$(C_{13}H_{19}ON)_2,H_2PtCl_6,$$

crystallises in thick plates; the precipitate obtained on addition of gold chloride to the solution of the hydrochloride contained less gold than required by the formula $C_{13}H_{19}ON,HAuCl_4$. The *nitroso*-derivative, $C_{13}H_{18}O_2N_2$, crystallises in thin, white plates and melts at 108—111°.

2-*Phenyl*-3 : 4 : 4 : 6-*tetramethyltetrahydro*-1 : 3-*oxazine*, obtained from methyldiacetonalkamine and benzaldehyde, is a yellow, mobile oil, which boils at 267—270° under 747 mm. pressure; the *aurichloride*, $C_{14}H_{21}ON,HAuCl_4$, crystallises in thin needles and melts and decomposes at 164—167°; the *platinichloride*, $(C_{14}H_{21}ON)_2,H_2PtCl_6$, forms glistening prisms. G. Y.

Oxazine Derivatives of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 153517).—3-Halogen-1-arylamino-2-hydroxyanthraquinones, prepared by replacing the 1-halogen atom in 1 : 3-dibromoxanthopurpurin, tetrabromoanthraflavic acid, tetrabromoanthrachrysone, &c., by arylamino-residues, are converted into oxazine derivatives by removal of hydrogen haloid on heating alone or with organic or inorganic bases. Or the process may be completed in one operation, a bromohydroxyanthraquinone, for instance, being heated with an aromatic amine.

3-*Bromo*-1-p-*toluidino*-2 : 4-*dihydroxyanthraquinone*, from 1 : 3-dibromoxanthopurpurin and *p*-toluidine, dissolves in concentrated sulphuric acid to a yellow solution, and in sodium hydroxide to a blue solution, and yields an oxazine on heating with heavy petroleum, sodium acetate, or a mixture of sodium acetate with acetic acid or aniline. C. H. D.

Connection between the Fluorescence and Chemical Constitution of Derivatives of Benzoxazole. FERDINAND HENRICH and GUSTAV OPFERMANN (*Ber.*, 1904, 37, 3108—3111).—It has previously been shown (Abstr., 1899, i, 171) that 5-hydroxy-1-phenyl-3-methylbenzoxazole, $\begin{array}{l}CH{:}CMe{\cdot}C{\cdot}N\\ \;|\qquad\quad\;\; ||\\ OH{\cdot}C{=}CH{-}C{-}O\end{array}\!\!>\!CPh$, when dissolved in concentrated sulphuric acid, is strongly fluorescent, whereas 3-hydroxy-5-methylbenzoxazole and its 1-methyl derivative are not so. That the fluorescence is not due merely to the magnitude of the radicle in position 1 is now shown by the fact that 5-*hydroxy*-3-*methyl*-1-*hexylbenzoxazole* is also not fluorescent; this substance, prepared by condensing *o*-amino-orcinol with heptoyl chloride, crystallises from light petroleum in yellowish-white needles and melts at 99°.

The 5-*benzoyl* and 5-*methyl* derivatives of 5-hydroxy-1-phenyl-3-methylbenzoxazole are also not fluorescent, and the same is true of 3-hydroxy-1-phenyl-5-methylbenzoxazole.

5-*Methoxy*-1-*phenyl*-3-*methylbenzoxazole*, prepared by methylating the hydroxy-compound, crystallises from dilute alcohol in needles and melts at 98°. 3-*Hydroxy*-1-*phenyl*-5-*methylbenzoxazole*, prepared by condensing 3 : 5-dihydroxy-*p*-toluidine with benzoyl chloride, crystallises from light petroleum and melts at 124—126°.

3-*Hydroxy*-1-*phenylbenzoxazole*, prepared from 2-aminoresorcinol, crystallises from benzene in nodular aggregates and melts at 138—139°. W. A. D.

Oxidation Products from *p*-Phenylenediamine. II. ERNST ERDMANN (*Ber.*, 1904, 37, 2906—2913. Compare this vol., i, 778).—Hydrogen peroxide oxidises *p*-phenylenediamine according to the equation: $3C_6H_8N_2 + 3H_2O_2 = C_{18}H_{18}N_6 + 6H_2O$. The base obtained, tetra-aminodiphenyl-*p*-azophenylene, crystallises in brown needles and melts at 242—243° (compare Bandrowski, Abstr., 1894, i, 236, and Willstätter, this vol., i, 511). Lead peroxide forms quinonedi-imide as the principal product. The latter compound is highly poisonous.

C. H. D.

Immedial-pure-blue. II. ROBERT GNEHM and FELIX KAUFLER (*Ber.*, 1904, 37, 3032—3033).—The tetrabromodimethylaminothiazone obtained on brominating immedial-pure-blue (this vol., i, 687) has now been prepared from Bernthsen's methylene-violet, and the identity of the two products proved by measurement of the absorption bands in various solvents.

E. F. A.

Action of Iodine and of Halogenated Substances on the Metallic Derivatives of Dibenzoylhydrazide. ROBERT STOLLÉ and ALFRED BENRATH (*J. pr. Chem.*, 1904, [ii], 70, 263—280. Compare Abstr., 1900, i, 531).—The *sodium* derivative of *s*-dibenzoylhydrazide, N_2HNaBz_2, crystallises in yellow needles; the *mercuric* derivative, $C_{14}H_{10}O_2N_2Hg$ (?), the *mercuric chloride* derivative,

$$HgCl \cdot N_2HBz_2,$$

and the *lead* derivative, $(N_2HBz_2)_2Pb$, are obtained as white precipitates; the *basic lead* derivative, $OHPb \cdot N_2HBz_2$, is yellow; when heated, the silver derivative yields diphenylfurodiazole.

When treated with sulphuric acid (3 vols. of acid, 1 vol. of water), azodibenzoyl yields nitrogen, hydrazine, and benzoic acid; with sodium ethoxide in alcoholic solution, it yields nitrogen *s*-dibenzoylhydrazide and benzoic acid; with water, at the ordinary temperature for two days, and finally warmed at 60°, it forms nitrogen, tribenzoylhydrazide, and a trace of *s*-dibenzoylhydrazide. The melting point of tribenzoylhydrazide varies greatly with the rate of heating; the melting point 198° (Stollé, this vol., i, 453) was due to slow heating, and not to the existence of a second tribenzoylhydrazide; when treated with sodium ethoxide in hot alcoholic solution, it yields the sodium derivative of *s*-dibenzoylhydrazide.

Acetyl-s-*dibenzoylhydrazide*, N_2HAcBz_2, formed by the action of acetyl chloride on dibenzoylhydrazide in ethereal solution, separates from alcohol in thick, colourless crystals, melts at 169—170°, and is hydrolysed by alkali hydroxides to *s*-dibenzoylhydrazide. *Ethyl* s-*dibenzoylhydrazidocarboxylate*, $N_2HBz_2 \cdot CO_2Et$, formed by the action of ethyl chlorocarbonate on the silver derivative of dibenzoylhydrazide, crystallises in matted, slender needles, melts at 130°, and yields dibenzoylhydrazide on hydrolysis with alkali hydroxides. *Ethyl hydrazido-carboxylate hydrochloride*, $N_2H_3 \cdot CO_2Et,HCl$, obtained by treating hydrazine hydrate with ethyl chlorocarbonate, forms hygroscopic crystals, melts at 129°, and, with benzaldehyde, yields Thiele and Lachmann's ethyl benzylidenehydrazidocarboxylate (Abstr., 1896, i, 208). Traube's ethyl dibenzoylhydrazidoacetate (Abstr., 1898, i,

235) is formed by the action of ethyl chloroacetate on the sodium derivative of *s*-dibenzoylhydrazide; the *silver* salt is obtained as a white precipitate; the *acid*, $N_2HBz_2 \cdot CH_2 \cdot CO_2H$, crystallises in small, flat, colourless prisms and melts and decomposes at 195°. Dibenzoylbenzylhydrazine (Curtius, Abstr., 1900, i, 611) is obtained by acting with benzyl chloride on the sodium derivative of *s*-dibenzoylhydrazide; it melts at 152°.

Dibenzoylethylhydrazine, N_2HEtBz_2, is formed along with diphenylfurodiazole when sodio-*s*-dibenzoylhydrazide is heated with ethyl bromide in a sealed tube at 130°. It crystallises with 2 mols. of water of crystallisation, melts at 100°, or when anhydrous, at 133°. *Dibenzoyl*-n-*propylhydrazine*, formed by the action of *n*-propyl bromide on sodio-*s*-dibenzoylhydrazide at 140°, crystallises in flat, glistening needles and melts at 131°. It is formed from *n*-propylhydrazine hydrochloride by the Schotten-Baumann reaction (compare Abstr., 1902, i, 57). The action of *n*-propyl bromide on dibenzoylhydrazide at 160° leads to the formation of the propyl ether of *s*-benzoylpropylhydrazine. It is obtained in the form of its *hydrobromide*,

$$C_{13}H_{20}ON_2,HBr,$$

which crystallises in slender needles and melts at 209°. The *ether*,

$$NHPr^{\alpha} \cdot N{:}CPh \cdot OPr^{\alpha},$$

crystallises in slender, silky needles, melts at 100°, and reduces ammoniacal silver solutions in presence of an alkali hydroxide.

G. Y.

Action of Phenylmethylhydrazine on Sugar. RUDOLF OFNER (*Ber.*, 1904, 37, 3362—3363. Compare this vol., i, 689).—Phenylmethylosazone, prepared by the action of phenylmethylhydrazine on dextrose, melts at 153° and is identical with the product obtained by Fischer from glucosone, and by Neuberg (Abstr., 1902, i, 264, 660) from *d*-fructose. It may also be prepared from phenylmethylhydrazine and dextrose-phenylmethylhydrazone. When phenylmethylhydrazine, which has undergone partial decomposition into phenylhydrazine, is used, phenylmethylphenylglucosazone, melting at 192—195°, is also formed.

A. McK.

Coupling of Acid Hydrazides with Sugars. RICHARD KAHL (*Zeit. Ver. Deut. Zucker-Ind.*, 1904, 1091—1119).—By the action of various acid hydrazides on sugars of the aldose type, the author has been enabled to prepare derivatives of these sugars which are insoluble or sparingly soluble in most solvents, and from which the original sugars may readily be obtained.

Dextrose-p-*bromobenzoylhydrazone*, $C_6H_{12}O_5{:}N \cdot NH \cdot CO \cdot C_6H_4Br$, prepared from dextrose and *p*-bromobenzoylhydrazide best in acetic acid solution, is insoluble in all the ordinary solvents, but extremely soluble in pyridine, from which ether precipitates it in white flocks; it has no true melting point, but chars at 200—202° when slowly heated, or at 206—207° when the heating is rapid. When gently heated with dilute sulphuric acid, it yields hydrazine sulphate, dextrose, and *p*-bromobenzoic acid, the last of which separates out almost completely in the solid state. The dextrose may also be recovered by

boiling the *p*-bromobenzhydrazide in water with a slight excess of benzaldehyde. Dextrose cannot be estimated by means of this compound, the highest yield of which was found to be 80 per cent.

No *p*-bromobenzhydrazide derivatives of lævulose, sucrose, maltose, and lactose could be prepared. The formation of the *p*-bromobenzhydrazone can hence be employed as a means of detection of an aldose in presence of large quantities of ketoses or bioses.

l-*Arabinose*-p-*bromobenzoylhydrazone*, $C_5H_{10}O_4:N \cdot NH \cdot CO \cdot C_6H_4Br$, forms a crystalline precipitate insoluble in all ordinary solvents, slightly soluble in cold pyridine, and more so on heating. When rapidly heated, it decomposes at 215—216°. It is decomposed by boiling water in presence of benzaldehyde, yielding a solution from which the arabinose can be crystallised.

Xylose-p-*bromobenzoylhydrazone* is insoluble in all solvents except pyridine, which resolves it into its constituents. It decomposes at 258—260°.

d-*Mannose*-p-*bromobenzoylhydrazone*, $C_6H_{12}O_5:N \cdot NH \cdot CO \cdot C_6H_4Br$, separates in microscopic, flat prisms, which are insoluble in the ordinary solvents, slightly soluble in pyridine in the cold, and extremely so in the hot, part of the compound being thus decomposed. It is readily resolved into its components by boiling water and decomposes at 205° when rapidly heated.

d-*Galactose*-p-*bromobenzoylhydrazone*, $C_6H_{12}O_5:N \cdot NH \cdot CO \cdot C_6H_4Br$, forms hard, microscopic prisms insoluble in the ordinary solvents and decomposed by pyridine. It is readily resolved by boiling water and decomposes at 216°.

p-*Chlorobenzoylhydrazide*, $C_6H_4Cl \cdot CO \cdot NH \cdot NH_2$, prepared by the action of hydrazine on ethyl *p*-chlorobenzoate in aqueous-alcoholic solution, separates from water as a felted mass of fine needles melting at 163°. It dissolves readily in alcohol, and reduces ammoniacal silver solution in the cold and Fehling's solution on boiling.

Dextrose-p-*chlorobenzoylhydrazone*, $C_6H_{12}O_5:N \cdot NH \cdot CO \cdot C_6H_4Cl$, prepared by the interaction of dextrose and *p*-chlorobenzoylhydrazide in alcoholic solution, is insoluble in the ordinary solvents and is decomposed by boiling with alcohol; on heating, it decomposes at 211°.

l-*Arabinose*-p-*chlorobenzoylhydrazone*, $C_5H_{10}O_4:N \cdot NH \cdot CO \cdot C_6H_4Cl$, is slowly dissolved and decomposed by boiling alcohol or cold pyridine; its decomposition temperature is 203°.

Salicylhydrazide, $OH \cdot C_6H_4 \cdot CO \cdot NH \cdot NH_2$, prepared by the action of hydrazine hydrate on ethyl salicylate in alcoholic solution, separates from aqueous solution in long prisms, which dissolve slightly in ether and more readily in benzene, alcohol, or acetic acid, and melt at 147°; it reduces ammoniacal silver solution in the cold and Fehling's solution on heating.

Dextrosesalicylhydrazone, $C_6H_{12}O_5:N \cdot NH \cdot CO \cdot C_6H_4 \cdot OH$, is extremely insoluble and readily decomposable; on heating, it decomposes at 198°.

l-*Arabinosesalicylhydrazone*, $C_5H_{10}O_4:N \cdot NH \cdot CO \cdot C_6H_4 \cdot OH$, crystallises in microscopic prisms decomposing at 191°; cold water or boiling alcohol gradually decomposes it.

Gallic hydrazide, $C_6H_2(OH)_3\cdot CO\cdot NH\cdot NH_2$, obtained by the interaction of ethyl gallate and hydrazine hydrate, forms a crystalline powder which reduces ammoniacal silver solutions in the cold and Fehling's solution on heating, and decomposes at 295—298°. On account of its great insolubility, its sugar derivatives could not be prepared.

Dextrose-β-naphthylsulphonhydrazone, $C_6H_{12}O_5:N\cdot NH\cdot SO_2\cdot C_{10}H_7$, forms a white, sandy precipitate consisting of microscopic prisms; boiling water rapidly and completely converts it into dextrose and the hydrazone.

l-*Arabinose-β-naphthylsulphonhydrazone*, $C_5H_{10}O_4:N\cdot NH\cdot SO_2\cdot C_{10}H_7$, forms a white powder which decomposes at 175° and dissolves to a slight extent in hot alcohol.

Owing to the extremely slight solubilities and ready preparation of the two preceding compounds, the use of β-naphthylsulphonhydrazide for the isolation of dextrose and arabinose is especially recommended.

Attempts to prepare compounds of dextrose with the hydrazides of palmitic, phenylacetic, and phenylpropionic acids were unsuccessful.

Rhamnosesemicarbazone, $C_6H_{12}O_4:N\cdot NH\cdot CO\cdot NH_2$, crystallises from aqueous alcohol in glassy, microscopic prisms decomposing at 169—170°; it is soluble in water and slightly so in alcohol. It is resolved into its components by boiling water in presence of benzaldehyde.

d-*Galactosesemicarbazone*, $C_6H_{12}O_5:N\cdot NH\cdot CO\cdot NH_2$, is deposited from aqueous alcohol in flat, glassy prisms decomposing at 186—189°; it is moderately soluble in water and slightly so in alcohol.

d-*Mannosesemicarbazone*, $C_6H_{12}O_5:N\cdot NH\cdot CO\cdot NH_2$, crystallises from aqueous alcohol in clear, hygroscopic, microscopic prisms and is soluble in water and very slightly so in alcohol.

Semicarbazide does not react with sugars of the ketose type, as is shown by observing the rotatory power of the solutions at intervals extending over a long period of time. T. H. P.

Synthesis of a Piperazine Derivative by the Polymerisation of Chloroethylamine and Decomposition of the Quaternary Salts of Piperazine by Alkalis. Ludwig Knorr (*Ber.*, 1904, 37, 3507—3519).—*Dimethylchloroethylamine*, $NMe_2\cdot C_2H_4Cl$, prepared by heating dimethylethanolamine with fuming hydrochloric acid at 170—180°, decomposing the hydrochloride formed with concentrated potassium hydroxide, and extracting with ether, forms a clear oil boiling at 109—110°. The *hydrochloride* crystallises from alcohol in large prisms and darkens and melts at 201°; the *aurichloride* forms long prisms and melts at 140°, previously sintering. Boiling alkali hydroxides decompose the base into dimethylethanolamine and tetramethylethylenediamine, acetylene being evolved: $4NMe_2\cdot C_2H_4Cl \longrightarrow NMe_2\cdot C_2H_4\cdot NMe_2 + C_2H_2 + 2NMe_2\cdot C_2H_4\cdot OH$. The salts of tetramethylethylenediamine have been described by Freund (Abstr., 1897, i, 495); the *base* forms a volatile oil, boiling at 120—122° under 745 mm. pressure.

The oily dimethylchloroethylamine polymerises rapidly, yielding a white, neutral, crystalline mass of *N*-dimethylpiperazine dimetho-

chloride, $2NMe_2{\cdot}C_2H_4Cl = NMe_2Cl{<}{\begin{smallmatrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{smallmatrix}}{>}NMe_2Cl$ (compare Gabriel, Abstr., 1896, i, 121; Marckwald and Frobenius, Abstr., 1902, i, 22). The same product is obtained by heating together tetramethylethylenediamine and ethylene chloride in alcoholic solution, and by decomposing synthetical 1 : 4-dimethylpiperazine dimethiodide with silver oxide and evaporating with hydrochloric acid. It decomposes above 300° into methyl chloride and 1 : 4-dimethylpiperazine. The *platinichloride* crystallises from boiling water in slender, orange needles and decomposes at 270°; the *aurichloride* forms golden leaflets and decomposes at 220°; the *picrate* forms insoluble, yellow crystals and decomposes at about 280°; the *ferrocyanide* forms a white, crystalline precipitate.

1 : 4-Dimethylpiperazine, prepared by distilling the above methochloride or by methylating piperazine by means of potassium methyl sulphate, boils at 131—132° under 752 mm. pressure (compare Schmidt and Wichmann, Abstr., 1892, i, 210).

Boiling alkali hydroxides decompose 1 : 4-dimethylpiperazine dimethochloride into tetramethylethylenediamine and dimethylethanolamine. The latter products are therefore not derived directly from dimethylchloroethylamine in the experiments described above, but from the piperazine derivative formed as an intermediate product. C. H. D.

Aminopyrazoles. LUDWIG KNORR (*Ber.*, 1904, 37, 3520—3525).—4-Aminopyrazole is readily prepared by reducing nitropyrazole with zinc dust and acetic acid (compare Wollers and Behrend, Abstr., 1902, i, 843). The *picrate* melts at 193—194° and contains 2 mols. of picric acid; the *picrolonate* melts at 242° and contains only 1 mol. of picrolonic acid. The *base* may be obtained by evaporation in an atmosphere of hydrogen, or by adding sodium hydroxide to a solution of a salt covered with a layer of ethyl acetate in an atmosphere of hydrogen, and may be sublimed in hydrogen, forming snow-white crystals melting at 80—82°. It is very hygroscopic, and dissolves in water to a neutral solution, which only darkens slowly in the air. Alkaline solutions readily absorb oxygen.

4-Aminopyrazole forms very stable diazonium salts, which are not decomposed by boiling water and form azo-dyes in the normal manner. Warm potassium iodide solution converts them into 4-iodopyrazole.

[With H. PEMSEL.]—3-(or 5)-*Aminopyrazole* may be prepared from pyrazole-3-(5)-carboxylic acid by successive conversion into the ethyl ester, hydrazide, azoimide, and urethane. These compounds will be described elsewhere. 3-(5)-Aminopyrazole forms a colourless, viscous, hygroscopic oil, boiling at 282° under 753 mm. pressure or at 218° under 122 mm., and dissolving readily in water, alcohol, or ethyl acetate, sparingly in ether. The aqueous solution is neutral; very little oxidation takes place in alkaline solution. The diazonium salts resemble those of 4-aminopyrazole.

[With PAUL MORENTZ.]—3 : 5-*Diaminopyrazole*, prepared in a similar manner from pyrazole-3 : 5-dicarboxylic acid (Abstr., 1894, i, 543),

forms a yellow, uncrystallisable syrup, readily soluble in water or alcohol, insoluble in ether. Nitrous acid forms diazonium compounds. Boiling dilute acids or alkalis decompose the base.

The *dibenzoyl* derivative melts at 207—208°, previously sintering.

All three amino-bases reduce solutions of gold salts. C. H. D.

5-Chloro-4-amino-1-phenyl-3-methylpyrazole. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 153861).—Zinc dust and sodium hydroxide reduce 5-chloro-1-phenyl-3-methylpyrazole-4-azobenzene to 1-phenyl-3-methylpyrazole-4-azobenzene (Michaelis and Leonhardt, this vol., i, 124). Acid reducing agents, however, reduce the azo-group without removing the chlorine, forming 5-*chloro*-4-*amino*-1-*phenyl*-3-*methylpyrazole*, which crystallises from light petroleum in tablets, melts at 49°, and dissolves readily in alcohol or ether. The *hydrochloride* crystallises from alcohol in tablets, decomposes at 220°, and yields a diazonium compound with nitrous acid.

Methylating agents and an alkali hydroxide form phenyldimethyldimethylaminopyrazolone.

1-*Phenyl*-3-*methylpyrazolone*-4-*azo*-o-*toluene*, from diazotised *o*-toluidine and phenylmethylpyrazole, forms red needles and melts at 183°. Phosphorus oxychloride at 100° converts it into 5-*chloro*-1-*phenyl*-3-*methylpyrazole*-4-*azo*-o-*toluene*, crystallising in orange needles and melting at 97°.

Similar compounds may be prepared from *p*-phenetidine. 1-*Phenyl*-2-*methylpyrazolone*-4-*azo*-p-*phenetole* forms orange needles and melts at 159°. 5-*Chloro*-1-*phenyl*-2-*methylpyrazole*-4-*azo*-p-*phenetole* forms orange leaflets and melts at 123°. C. H. D.

1-Phenyl-3 : 4 : 5-trimethylpyrazole. JAMES MCCONNAN (*Ber.*, 1904, 37, 3525—3528).—The properties of 1-phenyl-3 : 4 : 5-trimethylpyrazole given by Knorr and Jochheim (Abstr., 1903, i, 528) differ considerably from those given by Posner (Abstr., 1902, i, 83). The values found by the author for the boiling point of the base, the melting points of the picrate and aurichloride, and the decomposing point of the platinichloride are identical with those obtained by Knorr and Jochheim. The hydrochloride melts at about 90°, and the *picrolonate* decomposes at 120°. Posner's phenyltrimethylpyrazole probably contained some phenyldimethylpyrazole.

C. H. D.

Pyrimidines : 4 : 6-Diamino-2-oxypyrimidine. HENRY L. WHEELER and GEORGE S. JAMIESON (*Amer. Chem. J.*, 1904, 32, 342—357).—2-*Methylthiol*-4 : 6-*dioxypyrimidine* (2-*methylthiolbarbituric acid*), $NH<\substack{C(SMe):N \\ CO—CH_2}>CO$, obtained by the action of methyl iodide on thiobarbituric acid in presence of sodium ethoxide, crystallises in needles, is sparingly soluble in hot water and less so in alcohol, does not melt below 300°, but gradually assumes a pale brown colour. When this substance is heated with phosphorus pentachloride or oxychloride, it is converted into 4 : 6-*dichloro*-2-*methylthiolpyrimidine*, $N\leqslant\substack{C(SMe):N \\ CCl—CH}\geqslant CCl$, which boils at 135—136° under 14 mm. pressure,

crystallises in prisms, melts at 41—42°, and is readily soluble in ether, alcohol, or light petroleum.

4-*Chloro-6-amino-2-methylthiolpyrimidine*, $N\leqslant\begin{matrix}C(SMe)=N\\C(NH_2)\cdot CH\end{matrix}\geqslant CCl$, obtained by heating 4 : 6-dichloro-2-methylthiolpyrimidine with alcoholic ammonia for 4 hours at 125—126° in a sealed tube, crystallises in colourless needles, melts at 127—128°, and is sparingly soluble in water; when this substance is heated with alcoholic ammonia in a sealed tube for 2 hours at 185—190° and 4 hours at 215—220°, it is converted into 2 : 4 : 6-triaminopyrimidine (Gabriel, Abstr., 1902, i, 59). By the action of concentrated hydrochloric acid on 4-chloro-6-amino-2-methylthiolpyrimidine, 4-*chloro-6-amino-2-oxypyrimidine* (4-*chlorocytosine*), $N\leqslant\begin{matrix}CO-\!\!-\!\!-NH\\C(NH_2)\cdot CH\end{matrix}\geqslant CCl$, is produced, which crystallises from hot water in aggregates of small, slender prisms and does not melt at 300° but sinters and gradually becomes red; when this compound is heated with alcoholic ammonia, a *substance* is produced which forms small crystals, does not melt below 307°, is sparingly soluble in water, and contains 24·9 per cent. of nitrogen and no chlorine.

4 : 6-*Diamino-2-methylthiolpyrimidine*, $N\leqslant\begin{matrix}C(SMe)=N\\C(NH_2)\cdot CH\end{matrix}\geqslant C\cdot NH_2$, prepared by the action of methyl iodide on 4 : 6-diamino-2-thiopyrimidine, crystallises from hot water in slender prisms and melts and decomposes at 185—186°. When this substance is heated with concentrated hydrochloric acid, methyl mercaptan is evolved, and 4 : 6-*diamino-2-oxypyrimidine*, $NH<\begin{matrix}CO-\!\!-\!\!-\!\!-N\\C(NH_2):CH\end{matrix}>C\cdot NH_2$, is produced, which crystallises in slender, rectangular prisms, is sparingly soluble in hot water, becomes yellow at 297° and remains unmelted at 347°; its *hydrochloride* and *picrate* are described. If the treatment with hot hydrochloric acid is continued after the whole of the mercaptan has been expelled, the 4 : 6-diamino-2-oxypyrimidine is completely converted into barbituric acid. This diamino-oxypyrimidine is not identical with the base obtained by Kutscher from the nucleic acid of yeast (Abstr., 1903, i, 668), which is probably 5 : 6-diamino-2-oxypyrimidine.

5-iso*Nitroso-4 : 6-dioxy-2-methylthiolpyrimidine* (*2-methylthiolvioluric acid*), $NH<\begin{matrix}C(SMe)=N\\CO\cdot C(NOH)\end{matrix}>CO$, obtained by the action of nitrous acid on 2-methylthiol-4 : 6-dioxypyrimidine, crystallises with $2H_2O$ in red, flat, pointed prisms. When this substance is reduced with ammonium sulphide, 5 *amino-4 : 6-dioxy-2-methylthiolpyrimidine* (*2-methylthioluramil*), $NH<\begin{matrix}C(SMe)=\!\!=N\\CO\cdot CH(NH_2)\end{matrix}>CO$, is produced, which becomes brown at 285°, remains unmelted at 301°, and is sparingly soluble in water or hydrochloric acid.

2-*Thio-4 : 6-dioxy-5-methylpyrimidine* (*2-thio-5-methylbarbituric acid*), $NH<\begin{matrix}CS-\!\!-NH\\CO\cdot CHMe\end{matrix}>CO$, prepared by heating ethyl methylmalonate with thiocarbamide in presence of sodium ethoxide, forms thin plates

and melts and decomposes at about 244°; the compound crystallises with $1H_2O$, which is evolved at 120°. 2-*Thio*-4 : 6-*dioxy*-5-*ethylpyrimidine* (2-*thio*-5-*ethylbarbituric acid*) crystallises from water in long, acicular prisms, melts at 190—191°, and is soluble in alcohol. When an alcoholic solution of 2-methylthiolbarbituric acid is heated with methyl iodide, 4 : 6-*dioxy*-2-*methylthiol*-5-*methylpyrimidine*,

$$NH<\begin{matrix}C(SMe):N\\CO\cdot CHMe\end{matrix}>CO,$$

is produced, which crystallises from acetic acid in short prisms, decomposes at about 303°, and is almost insoluble in water or alcohol. 4 : 6-*Dioxy*-2-*methylthiol*-5-*ethylpyrimidine* crystallises from acetic acid, melts and decomposes at about 257°, and is readily soluble in alcohol and sparingly so in water.

4 : 6-*Dichloro*-2-*methylthiol*-5-*methylpyrimidine*,

$$N<\begin{matrix}C(SMe):N\\CCl{-}CMe\end{matrix}>CCl,$$

obtained by the action of phosphorus pentachloride on 4 : 6-dioxy-2-methylthiol-5-methylpyrimidine, boils at 153—154° under 18 mm. pressure, crystallises in stout, colourless prisms, and melts at 64°; when warmed with sodium ethoxide, it is converted into 4-*chloro*-6-*ethoxy*-2-*methylthiol*-5-*methylpyrimidine*, $N<\begin{matrix}C(SMe)=N\\C(OEt)\cdot CMe\end{matrix}>CCl$, which crystallises from alcohol in colourless prisms, melts at 85°, and is readily soluble in alcohol or benzene, but insoluble in water. 4-*Chloro*-6-*methylamino*-2-*methylthiol*-5-*methylpyrimidine*,

$$N<\begin{matrix}C(SMe)=\!=\!=N\\C(NHMe)\cdot CMe\end{matrix}>CCl,$$

obtained by heating 4 : 6-dichloro-2-methylthiol-5-methylpyrimidine with an alcoholic solution of methylamine, crystallises from alcohol in thick prisms and melts at 157°.

5-*Dimethylaminouracil*, $NH<\begin{matrix}CO{-}{-}{-}NH\\CO\cdot C(NMe_2)\end{matrix}>CH$, prepared by the action of dimethylamine on 5-bromouracil, crystallises from water in small, thin, colourless plates and melts and decomposes at about 297°. 5-*Methylamino*-4-*methyluracil*, $NH<\begin{matrix}CO{-}{-}{-}NH\\CO\cdot C(NHMe)\end{matrix}>CMe$, obtained by heating 5-bromo-4-methyluracil with aqueous methylamine, crystallises in colourless prisms with $1H_2O$ and melts at 214°; its *hydrochloride* melts and decomposes at 273°.

2-*Methylthiol*-4 : 6-*dimethylpyrimidine*, $N<\begin{matrix}C(SMe)\cdot N\\CMe{=}CH\end{matrix}>CMe$, prepared by the condensation of acetylacetone with the methyl iodide additive compound of thiocarbamide in presence of potassium hydroxide, boils at 135—137° under 28—29 mm. pressure, melts at 23—24°, and is fairly soluble in water; another *substance* is produced in this reaction, which crystallises from alcohol in colourless, rectangular prisms and melts at 153—154°. 4 : 6-Dimethyl-2-oxypyrimidine melts at 198—199° (compare Evans, Abstr., 1902, i, 111). E. G.

Behaviour of the Group N·C·N towards Acylating Agents. GUSTAV HELLER [and A. KÜHN] (*Ber.*, 1904, 37, 3112—3119).—On

adding benzoyl chloride to a solution of glyoxaline in pyridine, the glyoxaline ring is broken, dibenzoyldiaminoethylene being formed; with benzoic acid and sodium benzoate, glyoxaline gives only the *benzoate*, $C_{10}H_{10}O_2N_2$, which crystallises from ether and melts at 99°.

Benziminazole and β-naphthiminazole with benzoyl chloride in pyridine solution readily give the corresponding benzoyl derivatives; but when benziminazole is heated with acetic anhydride and sodium acetate, *o*-diacetylaminobenzene is obtained.

Diphenylformamidine, when acetylated according to Liebermann's method, gives only acetanilide; on benzoylation in benzene solution, *diphenylformamidine dibenzoate*, $C_{27}H_{24}O_4N_2$, melting at 177—178°, is the sole product.

Di-*p*-toluidinomethane is readily acetylated or benzoylated; the *dibenzoyl* derivative, $CH_2(NBz\cdot C_6H_4Me)_2$, is comparatively unstable, and on being heated with dilute hydrochloric acid gives principally benzo-*p*-toluidide. *Dibenzoyldi*-p-*phenetidylmethane* melts at 83—84°.

Dihydro-orexine (phenyltetrahydroquinazoline), when mixed with benzoyl chloride in pyridine, gives *o*-benzoylaminobenzylaniline, $NHBz\cdot C_6H_4\cdot CH_2\cdot NHPh$, and a small quantity of dibenzoylaminobenzylaniline. On acetylation, dihydro-orexine gives a product which does not crystallise.

Carbodi-*p*-tolylimide, on benzoylation, gives the additive compound *benzoyldi*-p-*tolylcarbamide*, $C_{22}H_{20}O_2N_2$, which crystallises from acetone and melts at 152—153°; some di-*p*-tolylcarbamide, melting at 260°, is also formed. On acetylation by Liebermann's method, acetyldi-*p*-tolylcarbamide is obtained; it melts at 148°, not at 140° as stated by Bamberger and Destraz (Abstr., 1902, i, 538).

Orexine (phenyldihydroquinazoline), on benzoylation in pyridine solution, gives an additive compound, 1-*benzoyl*-2-*benzoxy*-3-*phenyltetrahydroquinazoline*, $C_6H_4<\begin{matrix}NBz\cdot CH\cdot OBz\\ \quad\;\; | \\ CH_2\cdot NPh\end{matrix}$; it crystallises from alcohol or benzene in nodular aggregates of needles, melts at 168—169°, and on being heated with alcoholic potassium hydroxide gives a *substance* crystallising from benzene and melting at 116—117°.

W. A. D.

1-Acetylamino-2 : 4 diaminonaphthalene. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R-P. 151768).—1-*Acetylamino*-2 : 4-*diaminonaphthalene*, prepared by reducing 1-acetylamino-2 : 4-dinitronaphthalene (Meldola, Proc., 1886, 2, 172) with iron and acetic acid, crystallises in slightly brown needles, melts at 189°, and dissolves readily in alcohol or acetic acid, sparingly in benzene. It yields a golden-yellow dye on fusion with sulphur at 160°. C. H. D.

Bases of Triphenylmethane Dyes. ARTHUR HANTZSCH (*Ber.*, 1904, 37, 3434—3440. Compare Abstr., 1900, i, 365).—A reply to Baeyer and Villiger (this vol., i, 786). G. Y.

Nomenclature of the Rosanilines. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 504—505).—The author desires to amend the

nomenclature of the rosaniline bases, but considers Baeyer's nomenclature, in which the rosaniline bases are formulated as derivatives of fuchsonimine, too cumbersome. For pararosaniline, he proposes to substitute rosaniline. Rosaniline, magenta, new magenta, aniline-blue, and methyl-violet then become rosamonotoluidine, rosaditoluidine, rosatritoluidine, triphenylrosaniline, and hexamethylrosaniline respectively. H. M. D.

Tetrahydroxy*cyclo*hexanerosanilines—a New Class of Colourless Derivatives. Jules Schmidlin (*Compt. rend.*, 1904, **139**, 506—507. Compare this vol., i, 785).—The trihydrochlorides of the rosaniline bases combine with $4H_2O$ in acid solution and form, according to the author, tetrahydroxy*cyclo*hexanerosanilines analogous to the tetrachloro- and tetra-amino-*cyclo*hexanerosanilines previously obtained by the absorption of 4HCl or $4NH_3$. The hydrochlorides of magenta (rosaditoluidine) and of new magenta (rosatritoluidine) dissolve very readily in concentrated hydrochloric acid, and when kept for 24—48 hours the tetrahydroxy-compounds separate in the form of white crystals. They are stable at the ordinary temperature, but lose four molecules of water at 50°. They are very soluble in water; the concentrated solution slowly deposits magenta in the cold, immediately on warming. The fact that 4HCl, $4NH_3$, or $4H_2O$ are absorbed leads the author to conclude that the molecule of the rosaniline salts contains four double aliphatic bonds.

H. M. D.

Carbinol Salts and *cyclo*Hexanerosanilines; Decolorisation Phenomena. Jules Schmidlin (*Compt. rend.*, 1904, **139**, 521—524). —To explain the formation of colourless solutions when the trihydrochlorides of the rosaniline bases are dissolved in excess of mineral acid, it is assumed that four mols. of water are taken up, the quinonoid nucleus being transformed into a *cyclo*hexane ring (compare preceding abstract). This view is supported by thermochemical data. Hexamethylpararosaniline trihydrochloride dissolves in dilute hydrochloric acid giving a coloured solution which, however, soon becomes colourless. During the colour change, 5 cal. are developed. Compared with the total heat change in this case, the heat of solution of the corresponding carbinol trihydrochloride is greater by 5 cal., whilst that of the *cyclo*hexane trihydrochloride is less to the extent of 5 cal. These data do not accord with the view that carbinol salts are present in solution.

It seems probable that, when the rosaniline-carbinols are neutralised by acid, the benzene ring first undergoes transformation into a *cyclo*hexane ring, which by loss of water gives rise to the quinonoid structure. H. M. D.

Thermochemical Comparison of Rosanilines and Leucanilines. Jules Schmidlin (*Compt. rend.*, 1904, **139**, 542—544).—The heats of neutralisation of the rosaniline-carbinols have been measured, and data are given for the formation of (I) the solid monohydrochlorides, (II) the solid trihydrochlorides. The heats of formation of the solid

leucaniline trihydrochlorides from the corresponding solid leuco-bases and aqueous hydrochloric acid are also recorded (III):

Carbinol bases.	I.	II.	III.
Pararosaniline (solid) + HCl (aq.)	+ 9·9 cal.	+ 16·1 cal.	+ 12·0 cal.
Rosaniline ,, ,,	9·6 ,,	16·4 ,,	12·4 ,,
Magenta C_{21} ,, ,,	10·9 ,,	16·3 ,,	13·1 ,,
New magenta ,, ,,	11·1 ,,	16·3 ,,	12·8 ,,
Hexamethyl-pararosaniline ,, ,,	13·7 ,,	18·2 ,,	14·3 ,,
,, ,, + HBr (aq.)	11·4 ,,	15·3 ,,	

It is found that the monohydrochlorides contain H_2O, which is only evolved at about 250°.

The heat development in the formation of the trihydrochlorides is in every case greater for the carbinol salt than for the leuco-salt. In the case of the carbinols, the first molecule of acid develops much more heat than the second or third, and this inequality increases with the strength of the base. The thermal data are in accord with the fact that the bases behave essentially as monoacid bases.

The heats of formation of the tetrahydroxy*cyclo*hexane salts from the rosaniline trihydrochlorides are:

Magenta C_{21} trihydrochloride	(solid)	+ $4H_2O$ (liq.)	=	+ 5·6 cal.
New magenta	,,	,,	=	5·5 ,,
Hexamethyl-pararosaniline	,,	,,	=	7·0 ,,

H. M. D.

Relations between the Safranines, Mauveines, Indulines, Indazines, Naphthyl-red, Naphthyl blue, Rosindulines and Magdala-red. LUDWIG PAUL (*Chem. Zeit.*, 1904, 28, 777—780).—A theoretical paper unsuitable for abstraction. W. A. D.

[Indophenol Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 152689).—Only small quantities of an unstable indophenol are obtained on oxidising a mixture of phenol and *p*-phenylenediamine. By dissolving phenol and 2 : 6-dichloro-*p*-phenylenediamine in very dilute hydrochloric acid and adding potassium dichromate, a stable *indophenol* is precipitated in the form of a red powder, becoming bronze-like on rubbing; it dissolves in organic solvents to red or violet solutions. A solution of sodium sulphide reduces it to the corresponding diphenylamine derivative, which forms colourless crystals dissolving in sodium hydroxide; the solution becoming oxidised to the indophenol on exposure to air. The *hydrochloride* forms slender, felted needles. C. H. D.

A New Reaction of the Semicarbazones. II. WALTHER BORSCHE and C. MERKWITZ (*Ber.*, 1904, 37, 3177—3187. Compare Abstr., 1902, i, 186).—The semicarbazones of acetone, acetophenone, benzophenone, *β*-methylhexanone, *l*-menthone, *d*-camphor, pulegone, and

d-carvone react in the normal manner with primary aromatic amines, for instance,
$CMePh{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_2Ar = CMePh{:}N{\cdot}NH{\cdot}CO{\cdot}NHAr + NH_3$; from the condensation products formed in this manner, the corresponding hydrazides may be obtained by means of dilute hydrochloric acid. The behaviour of the semicarbazones of benzylideneacetone, *o*-hydroxybenzylideneacetone, and methyl-*o*-hydroxybenzylideneacetone, on the other hand, is abnormal.

Benzophenonesemicarbazone, $CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, prepared from benzophenone and semicarbazide, separates from alcohol in needles, which become liquid at 164—165° and decompose at a higher temperature with the evolution of ammonia and formation of ammonium carbamate, hydrazodicarboxylamide, and benzophenoneazine. When boiled with aniline, it yields *benzophenonephenylcarbamic acid hydrazone*, $CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NHPh$, separating from alcohol in needles and melting at 163°.

3-*Methyl*cyclo*hexanonephenylcarbamic acid hydrazone*, prepared by boiling 3-methyl*cyclo*hexanonesemicarbazone with aniline, separates from alcohol in needles and melts at 169—170°.

l-*Menthonephenylcarbamic acid hydrazone*,

$$CH_2{<}{}^{CH_2-CHPr}_{CHMe\cdot CH_2}{>}C{:}N{\cdot}NH{\cdot}CO{\cdot}NHPh,$$

prepared from *l*-menthonesemicarbazone and aniline or by condensation of *l*-menthone with phenylcarbamic acid hydrazide, separates from alcohol in needles and melts at 180—181°.

d-*Camphorphenylcarbamic acid hydrazone*, $C_{10}H_{16}{:}N{\cdot}NH{\cdot}CO{\cdot}NHPh$, prepared from *d*-camphorsemicarbazone and aniline, becomes liquid at 153—154°. When warmed with dilute hydrochloric acid, it is converted into phenylsemicarbazide hydrochloride and *d*-camphor.

Pulegonephenylcarbamic acid hydrazone forms tiny needles melting at 132—133°.

d-*Carvonephenylcarbamic acid hydrazone* crystallises in needles and melts at 176—177°.

Benzylideneacetonephenylcarbamic acid hydrazone,

$$CHPh{:}CHMe{\cdot}C{:}N{\cdot}NH{\cdot}CO{\cdot}NHPh,$$

prepared from benzylideneacetone and semicarbazide, separates from alcohol in yellow leaflets and melts at 187°. When gently boiled with aniline for 8 minutes, it forms *benzylideneacetonephenylsemicarbazone*, which separates from alcohol in tiny needles and melts at 195°. When benzylideneacetonesemicarbazone is further boiled with aniline, diphenylcarbamide and a resin are produced; this resin, when treated with dilute hydrochloric acid and then distilled in steam, yields benzaldehyde, whilst the residue contains benzalazine.

o-*Hydroxybenzylideneacetonesemicarbazone*,

$$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

prepared from *o*-hydroxybenzylideneacetone and semicarbazide hydrochloride, forms yellow needles and melts and decomposes at 206—207°. The corresponding *phenylsemicarbazone* separates from alcohol in needles and melts and decomposes at 183—184°; the *benzoyl* derivative melts at 204—205°. By prolonged boiling with aniline, *o*-hydroxybenzylideneacetonesemicarbazone yields *s*-diphenylcarbamide as the main product,

o-hydroxybenzylideneazine being also formed; the latter melts at 213—214°, and was further identified by conversion into its diacetyl derivative, melting at 190—191°.

2-*Hydroxy-5-methylbenzylideneacetone*, prepared from 2-hydroxy-5-methylbenzaldehyde and acetone, melts at 128—129°. Its *semicarbazone* melts at 203°, and, when boiled with aniline, forms carbanilide, 2-hydroxy-5-methylbenzylideneacetonephenylsemicarbazone, and 2-*hydroxy-5-methylbenzylideneazine*. The latter separates from a mixture of chloroform and alcohol in glistening needles and melts at 122°, whilst its *diacetyl* derivative melts at 163°. 2-*Hydroxy-5-methylbenzylideneacetonephenylcarbamic acid hydrazone* separates from alcohol in leaflets and melts at 177°. A. McK.

Semicarbazones of Reducing Sugars. Léon Maquenne and W. Goodwin (*Bull. Soc. chim.*, 1904, [iii], 31, 1075—1078).—The semicarbazones were prepared by adding a slight excess of semicarbazide, dissolved in alcohol, to a solution of the sugar in water and setting the mixture aside for several days. The melting points recorded were determined on the Maquenne block (Abstr., 1904, ii, 383). The specific rotations quoted are for aqueous solutions.

Arabinosesemicarbazone forms small crystals, melts and decomposes at about 190°, dissolves in 6·5 parts of water at 20°, and has $[\alpha]_D$ +25° immediately after solution and +23·8° after 24 hours (compare Herzfeld, *Zeit. Ver. Rubenzuck. Ind.*, 1897).

Xylosesemicarbazone occurs in brilliant crystals, melts and decomposes at about 202—204°, dissolves in 4·65 parts of water at 21°, and has $[\alpha]_D$ −38·8° on solution, −26·3° after 24 hours, and −24·4° after 48 hours.

Rhamnosesemicarbazone, $C_7H_{15}O_5N_3,\frac{1}{2}H_2O$, was obtained in large crystals melting and decomposing at about 183°. The compound does not become anhydrous at 120°; it dissolves in 22·3 parts of water at 21°, has $[\alpha]_D$ +75° at the moment of solution, and +50° after 120 hours.

Dextrosesemicarbazone, $C_7H_{15}O_6N_3$, melts and decomposes at about 197—198°, dissolves in 50 parts of water at 21° and in 42·5 parts at 25°, and has $[\alpha]_D$ −17° some minutes after solution and −9° after 72 hours (compare Breuer, Abstr., 1898, i, 620).

Mannosesemicarbazone, $C_7H_{15}O_6N_3,\frac{1}{2}H_2O$, forms bulky crystals, melts at 117°, or when slowly heated at 108°, dissolves in 14·28 parts of water at 20·5°, and has $[\alpha]_D$ −53° at first, and −43° after 24 hours.

Galactosesemicarbazone occurs in small crystals and melts at about 200—202°. The aqueous solution, saturated at 20·5°, contains 8·9 grams per 100 c.c. The substance has $[\alpha]_D$ +3·1° at first, and +16·9° after 48 hours.

Lactosesemicarbazone, $C_{13}H_{25}O_{11}N_3,2H_2O$, was obtained in bulky crystals melting and decomposing at about 185°; it loses $1H_2O$ at 115° and a second at 120°, decomposing slightly at the same time. The solution in water, saturated at 20·5°, contains 19·8 grams in 100 c.c. The specific rotation $[\alpha]_D$ is +10·6° at first, and +11·25° after 24 hours.

Cellosesemicarbazone, $C_{13}H_{25}O_{11}N_3,2H_2O$, is a crystalline powder

which becomes anhydrous at 115°. Its saturated solution contains 7·2 grams in 100 c.c. at 21°. The substance has $[\alpha]_D$ – 7·8° at first, and – 5·2° after 48 hours. T. A. H.

Action of Phenylhydrazine on Benzoyl-ψ-thiocarbamides. 3-Amino-1 : 5-diphenylpyrro-αβ'-diazole [3-Amino-1 : 5-diphenyl-1 : 2 : 4-triazole] Derivatives. TREAT B. JOHNSON and GEORGE A. MENGE (*Amer. Chem. J.*, 1904, 32, 358—372. Compare Wheeler and Beardsley, Abstr., 1903, i, 293).—*Methyl benzoyliminothiolcarbonate*, NBz:C(SMe)·OMe, obtained by the action of methyl iodide on methyl benzoylthioncarbamate in presence of sodium ethoxide, boils at 200° under 20 mm. pressure, crystallises from light petroleum in colourless prisms, and melts at 43°. Benzoyl-*m*-nitrophenylmethyl-ψ-carbamide (Wheeler and Johnson, Abstr., 1900, i, 635) crystallises from alcohol in acicular prisms and melts at 86—88°.

Benzoyl-ψ-cumylmethyl-ψ-carbamide, $NBz:C(OMe)\cdot NH\cdot C_6H_2Me_3$, prepared from ψ-cumidine and methyl ethyl benzoyliminothiolcarbonate, crystallises from alcohol in needles, melts at 87—89°, and is readily soluble in ether or benzene. When this substance is heated with phenylhydrazine at 130°, 3-ψ-*cumylamino*-1 : 5-*diphenyltriazole*,

$$NPh{<}\begin{matrix}N{=}C\cdot NH\cdot C_6H_2Me_3\\ CPh{:}N\end{matrix},$$

is produced, which crystallises from alcohol in rosettes of needles and melts at 121—123°.

By the action of phenylhydrazine on benzoylphenylethyl-ψ-carbamide, 3-anilino-1 : 5-diphenyltriazole (Wheeler and Beardsley, *loc. cit.*) is produced.

Benzoyl-m-*nitrophenylethyl-ψ-carbamide*, $NBz:C(OEt)\cdot NH\cdot C_6H_4\cdot NO_2$, prepared from *m*-nitroaniline and ethyl benzoyliminothiolcarbonate, crystallises from alcohol in prisms and melts at 86—88°.

Benzoyl-m-*chlorophenylethyl-ψ-carbamide*, $NBz:C(OEt)\cdot NH\cdot C_6H_4Cl$, from *m*-chloroaniline and ethyl benzoyliminothiolcarbonate, crystallises from alcohol in long, slender prisms and melts at 47—48°; when heated with phenylhydrazine, it is converted into 3-m-*chlorophenylamino*-1 : 5-*diphenyltriazole*, $NPh{<}\begin{matrix}N{=}C\cdot NH\cdot C_6H_4Cl\\ CPh{:}N\end{matrix}$, which crystallises from alcohol in short, stout prisms and melts at 195—196°.

Benzoyl-p-*tolylethyl-ψ-carbamide*, $NBz:C(OEt)\cdot NH\cdot C_6H_4Me$, from *p*-toluidine and ethyl benzoyliminothiolcarbonate, crystallises in needles or prisms, melts at 77—78°, and, when heated with phenylhydrazine, yields 3-*p*-toluidino-1 : 5-diphenyltriazole (Wheeler and Beardsley, *loc. cit.*).

Benzoyl-p-*anisylethyl-ψ-carbamide*, $NBz:C(OEt)\cdot NH\cdot C_6H_4\cdot OMe$, from *p*-anisidine and ethyl benzoyliminothiolcarbonate, crystallises from alcohol in long, slender prisms and melts at 66—67°. By the action of phenylhydrazine on this compound, it is converted into 3-p-*anisylamino*-1 : 5-*diphenyltriazole*, $NPh{<}\begin{matrix}N{=}C\cdot NH\cdot C_6H_4\cdot OMe\\ CPh{:}N\end{matrix}$, which crystallises from alcohol in slender prisms and melts at 224—225°.

Benzoyl-ψ-cumylethyl-ψ-carbamide, $NBz:C(OEt)\cdot NH\cdot C_6H_2Me_3$, from

ψ-cumidine and ethyl benzoyliminothiolcarbonate, crystallises in prisms and melts at 79—80°.

By the action of phenylhydrazine on benzoyl thiocyanate in ethereal solution, benzoylphenylthiosemicarbazide (m. p. 136°), 3-thiol-1 : 5-diphenyltriazole, and 5-thiol-1 : 3-diphenyltriazole are produced (compare Dixon, Trans., 1889, 55, 304).

When acetonephenylhydrazone is heated with an ethereal solution of benzoyl thiocyanate, the *β-propylidene* derivative of benzoylphenylthiosemicarbazide, $NHBz{\cdot}CS{\cdot}NPh{\cdot}N{:}CMe_2$, is produced, which crystallises from alcohol in prisms, melts at 136°, and is converted by hydrochloric acid or boiling water into 5-thiol-1 : 3-diphenyltriazole.

By the action of ψ-thiocarbamide on ethyl benzoyliminothiolcarbonate at the ordinary temperature, mercaptan is produced together with *ethoxyethylthiolphenyl*-1 : 3 : 5-*triazine*,

$$N{<}\begin{matrix}C(SEt){\cdot}N\\C(OEt){:}N\end{matrix}{>}CPh,$$

which crystallises in prisms, melts at 47—48°, and is very stable.

When ethyl benzoyliminothiolcarbonate is treated with an alcoholic solution of hydroxylamine, mercaptan is evolved and 3-*ethoxy*-5-*phenyl*-1 : 2 : 4-*oxadiazole*, $\begin{matrix}C(OEt){:}N\\ | \quad\quad \\ N{=\!=}CPh\end{matrix}{>}O$, is formed, which crystallises from alcohol in thick prisms, melts at 47—48°, and is freely soluble in benzene, ether, or light petroleum. By the action of ethyl iodide on the silver salt of 5-hydroxy-3-phenyl-1 : 2 : 4-oxadiazole, 5-ethoxy-3-phenyl-1 : 2 : 4-oxadiazole, $\begin{matrix}CPh{=\!=}N\\ | \quad\quad \\ N{:}C(OEt)\end{matrix}{>}O$, is produced ; this compound was first obtained by Falck (Abstr., 1886, 797), who regarded it as a compound in which the ethyl group is attached to nitrogen.

Benzoyl iso*cyanochloride*, $C_6H_5{\cdot}CO{\cdot}N{:}CCl_2$, obtained by the action of chlorine on a solution of benzoyl thiocyanate in chloroform, is an oily liquid which boils at 146—148° under 31 mm. pressure, reacts readily with water, alcohols, or amines, has a very penetrating odour, and attacks the eyes. E. G.

Preparation of 8-Xanthinecarboxylic Acids. C. F. BOEHRINGER & SÖHNE (D.R.-P. 153121).—The 8-trichloromethylxanthines (this vol., i, 340) are hydrolysed to carboxylic acids, which readily lose carbon dioxide, so that the corresponding xanthines are generally obtained directly (this vol., i, 686). The reaction may be arrested at the first stage by boiling the chloro-compound with water for a short time, or by warming with sodium acetate, or by heating with alcohol and hydrolysing the resulting ester.

3-*Methyl*-8-*trichloromethylxanthine* crystallises from glacial acetic acid in prisms and decomposes above 300°. Boiling water converts it into 3-*methylxanthine*-8-*carboxylic acid*, crystallising from water in glistening leaflets containing $2H_2O$; the *ethyl* ester melts at 304—305° and the *methyl* ester at 290—291°.

8-Trichloromethylcaffeine yields caffeinecarboxylic acid (Gomberg, Abstr., 1895, i, 628).

Ethyl theobrominecarboxylate, from 8-trichloromethyltheobromine and

alcohol, forms felted needles and melts at 300°, the *methyl* ester melts at 270°. Potassium hydroxide forms *theobrominecarboxylic acid*, crystallising in short needles and melting at 345°. The *potassium* salt forms slender needles. C. H. D.

Preparation of 7′:8-Dichlorocaffeine. C. F. Boehringer & Söhne (D.R.-P. 153122).—7′:8-Dichlorocaffeine (this vol., i, 188) may be prepared by the action of dry chlorine on caffeine or 8-chlorocaffeine at 100—110°. C. H. D.

Oxidation of Uric Acid in Alkaline Solution. Robert Behrend (*Annalen*, 1904, 333, 141—160. Compare following abstract).—Since Fischer (Abstr., 1899, i, 392; 1900, i, 63) has shown that both 1- and 7-methyluric acids yield the same β-methylallantoin, and 3- and 9-methyluric acids the same α-methylallantoin, it has become obvious that in the oxidation of uric acid in an alkaline medium to allantoin, one of the five-membered rings is not simply broken, but that a more complicated process takes place, both rings being probably broken and one again regenerated.

Many experiments have been made with the object of throwing further light on the chemical changes involved in the oxidation of uric acid in alkaline solution. In the first place, the temperature and the amount of alkali were varied, the proportion of permanganate being kept constant, one atom of oxygen to 1 mol. of uric acid.

That allantoin is not the first product of the oxidation is shown by the fact that a solution of allantoin in cold dilute alkali hydroxide is completely decomposed in two days, whereas if the product of oxidation of uric acid, which is strongly alkaline, is kept for eight weeks, allantoin can still be readily isolated. All the allantoin is only destroyed after six days at a temperature of 35—40°; the strongly alkaline product of the oxidation can even be evaporated to dryness on the water-bath without all the allantoin being destroyed.

Another substance, uroxanic acid, is always formed together with allantoin when uric acid is oxidised by permanganate or oxygen in alkaline solution. The amount of alloxantoin varies only slightly with the concentration of the alkali and with the temperature, but the amount of uroxanic acid is largely dependent on the concentration of the alkali. When 3 mols. of potassium hydroxide are used for each mol. of uric acid, no uroxanic acid is formed; with increasing excess of the alkali, up to 5 or 6 mols., of the hydroxide to 1 mol. of uric acid, the yield of the acid increases to 23—24 per cent. of the theoretical; a further increase of the alkali is without influence. The amount of alkali is, however, without influence on the course of the oxidation, for it is immaterial to the yield of uroxanic acid whether the excess of alkali is added during the oxidation or only before the subsequent evaporation. One substance is formed by the oxidation, which is then converted into uroxanic acid by heating with the excess of alkali.

The uroxanic acid cannot be regarded as the original oxidation product of the uric acid, since it can be heated for many hours in the solution without undergoing any marked decomposition.

All the evidence then points to the view that a single substance is

formed on the oxidation of uric acid in alkaline solution, which on acidification with acetic acid is converted into allantoin, and on heating with excess of alkali hydroxide into uroxanic acid, but if evaporated in the absence of excess of alkali, is changed into other still unknown products. In certain experiments, it is shown that the sum of the allantoin and the uroxanic acid represent all the uric acid employed.

Although the constitution of uroxanic acid is not finally settled, it is very probably the diureide of malonic acid, $(NH_2\cdot CO\cdot NH)_2C(CO_2H)_2$. There is evidence (which will be published in a future communication) that the first product of oxidation of uric acid is hydroxyglycoluril-carboxylic acid, $CO<\begin{array}{l}NH\cdot C(CO_2H)\cdot NH\\ NH\cdot C(OH)—NH\end{array}>CO$; this is next converted into the compound $\begin{array}{l}NH\cdot CH(OH)\\ CO——NH\end{array}>C(OH)\cdot NH\cdot CO\cdot NH_2$, which then on acidification yields carbon dioxide and allantoin, or, on evaporation with alkali, takes up the elements of water with the production of uroxanic acid. K. J. P. O.

Constitution of β-Methylallantoin. LUDWIG SIEMONSEN (*Annalen*, 1904, 333, 101—141).—Since the constitution of both the α- and β-methylallantoins, which are obtained from 1- and 7-methyluric acids and from 3- and 9-methyluric acids respectively, is still in doubt, an attempt has been made to ascertain that of the β-compound by synthesis from methylhydantoin and carbamide.

To prepare hydantoin, the decomposition of glycoluril is recommended; the substance last mentioned is obtained by treating glyoxal (prepared by oxidising paraldehyde with nitric acid) with carbamide in the presence of hydrochloric acid; the glycoluril is best hydrolysed by boiling with concentrated hydrochloric acid, evaporating to a small bulk, and then adding alcohol, when the hydantoin crystallises out, a yield of 75 per cent. being obtained. Methylhydantoin was easily prepared in the usual manner, but dimethylhydantoin could not be obtained.

Attempts to prepare bromo-derivatives of hydantoin failed; the action of bromine is very slow in the absence of a carrier, such as iron wire; when $\frac{1}{2}$ mol. of bromine is used for each mol. of hydantoin, *iso-alliluric acid*, $CO<\begin{array}{l}NH\cdot CH\cdot N—CH_2\\ NH\cdot CO\ \ CO\cdot NH\end{array}>CO$, an oxidation product of hydantoin, is obtained in a yield of 84 per cent.; it crystallises in sparingly soluble prisms, which become coloured at 250° and melt and decompose at 258—260°. It can be boiled with concentrated nitric acid and is only attacked by boiling permanganate; ammonia is slowly evolved when it is boiled with concentrated potassium hydroxide. It dissolves readily in ammonia, the solution with silver nitrate giving a *silver* salt, $C_6H_4O_4N_4Ag_2$. This acid appears to be isomeric with Schlieper's alliluric acid (*Annalen*, 1845, 56, 20).

When larger proportions of bromine are used, parabanic acid is formed, the dibromo-derivative, $CO<\begin{array}{l}NH\cdot CBr_2\\ NH\cdot CO\end{array}$, being probably first produced.

Methylhydantoin is converted by bromine under all conditions into *aa-dimethylisoalliturie acid*, $CO<\begin{matrix}NH-CH\cdot N-CH_2 \\ NMe\cdot CO \quad CO\cdot NMe\end{matrix}>CO$, which crystallises in leaflets, fairly soluble in hot water and melting at 208—210°; it remains unchanged when heated with concentrated nitric acid.

β-Nitroisoalliturie acid, $C_6H_5O_4N_4\cdot NO_2$, cannot be prepared by boiling *iso*alliturie acid with nitric acid, but only by treatment with a mixture of nitric acid and phosphoric oxide at 50—60°; it forms a micro-crystalline powder melting and decomposing between 170° and 195° and is decomposed by heating with water, oxalic acid and hydantoin being produced. It dissolves in sodium hydroxide with a yellow coloration, acids precipitating oxaluric acid and hydantoin from the solution.

β-Nitro-aa-dimethylisoalliturie acid, prepared in the same manner as the nitro-compound last mentioned, crystallises in prisms melting and decomposing between 170° and 190°, and is decomposed when boiled with water into *a*-methylhydantoin, oxalic acid, nitric oxide, and carbon dioxide. It dissolves in alkali hydroxides with a yellow coloration and is thereby decomposed into methyloxaluric acid (which, on acidification, separates in prisms and melts and decomposes at 177—178°), *a*-methylhydantoin (m. p. 181—182°), oxalic acid, and nitrous acid.

β-Acetyl-aa-dimethylisoalliturie acid, $C_6H_3O_4N_4Me_2Ac$, prepared by boiling dimethyl*iso*alliturie acid with acetic anhydride, crystallises in leaflets melting at 193—194°.

Attempts to hydrolyse *iso*alliturie acid with concentrated hydrochloric acid led to the production of an amino-acid yielding a blue copper salt, but it could not be obtained pure.

aβ-Diacetylhydantoin, $CO<\begin{matrix}NAc\cdot CH_2 \\ NAc\cdot CO\end{matrix}$, is formed when hydantoin is boiled with acetic anhydride, and crystallises in leaflets melting at 104—105°; when boiled with water, it is converted into *β*-acetylhydantoin (m. p. 143—144°). *β-Acetyl-a-methylhydantoin*, prepared from *a*-methylhydantoin, crystallises in long needles melting at 134—135°.

When *aβ*-diacetylhydantoin is boiled with a solution of bromine in acetic acid, acetylhydantoin is alone formed; *β*-acetyl-*a*-methylhydantoin, on the other hand, is largely converted into *aa*-dimethyl*iso*alliturie acid (m. p. 208—210°), a fact which indicates that the two nuclei are linked together by the nitrogen atoms (compare above).

As the result of a long series of experiments, it was found that allantoin is best prepared from hydantoin and carbamide by boiling a solution of hydantoin (4 grams), bromine (6·4 grams), and carbamide (0·2 gram) in 25 c.c. of acetic acid, and after 10 minutes adding 3 grams of carbamide dissolved in 20 c.c. of acetic acid; the product is evaporated and the hydantoin extracted with alcohol. In a similar manner, *β*-methylallantoin was prepared from *a*-methylhydantoin and proved to be identical with the substance obtained by Fischer from 1- or 7-methyluric acid.

This synthesis shows that *β*-methylallantoin is represented by the formula $\begin{matrix}CO-NH \\ NMe\cdot CO\end{matrix}>CH\cdot NH\cdot CO\cdot NH_2$. K. J. P. O.

Certain Nitrogen Compounds. FREDERICK J. ALWAY and REUBEN M. PINCKNEY (*Amer. Chem. J.*, 1904, 32, 398—400).—m-*Nitrobenzene*-p-*azobenzaldehyde*, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CHO$, obtained by the condensation of *p*-nitrobenzaldehyde with *m*-nitroaniline in presence of acetic acid, forms orange-red, indistinctly crystalline masses, melts at 223°, and is sparingly soluble in alcohol or acetic acid.

Ethyl p-*nitrosobenzoate*, obtained by reducing ethyl *p*-nitrobenzoate with zinc dust and acetic acid and treating the product with chromic acid, crystallises in yellow needles, melts at 81°, and forms green solutions; ethyl *p*-azoxybenzoate (Meyer and Dahlem, Abstr., 1903, i, 448) is also produced in this reaction. E. G.

o-Hydroxyazo-Dye from 2:4-Dichloro-α-naphthylaminesulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 153298).—2 : 4-*Dichloro-α-naphthylaminesulphonic acid*, prepared by the action of fuming sulphuric acid on 2 : 4-dichloroacetyl-α-naphthalide, is a colourless powder, dissolving sparingly in water. The *sodium*, *zinc*, and *magnesium* salts form colourless crystals. The diazonium compound forms yellow dyes with resorcinol, &c., in alkaline solutions, but when solutions containing alkali acetates or carbonates are employed, deep violet dyes are obtained. In this case, the chlorine atom in the ortho-(β)-position is replaced by hydroxyl. The same result is obtained when the aminc-acid is treated with sodium nitrite without the addition of mineral acid. The violet dyes from resorcinol or β-naphthol yield fast blue-black shades on subsequent treatment with chromium salts. C. H. D.

Diazo-compounds [an Explanation]. ARTHUR HANTZSCH (*Ber.*, 1904, 37, 3030).—The author's criticisms (this vol., i, 201) referred to Euler's theoretical conclusions, and not to his experimental results. G. Y.

Diazotisation of Sulphonated *m*-Diamines. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 152879).—It has not been possible hitherto to diazotise one amino-group in sulphonated *m*-diamines. It may, however, be performed by mixing the diamine with the calculated quantity of alkali nitrite and then adding the mineral acid, or otherwise, so that the diamine is always in presence of the requisite quantity (1 mol.) of free nitrous acid. The diazotisation of several diaminosulphonic acids is described in detail. C. H. D.

Electrolytic Preparation of Azo-dyes. C. F. BOEHRINGER & SÖHNE (D.R.-P. 152926).—Azo-dyes may be prepared by electrolysing a solution of sodium nitrite containing an aromatic amine in solution or suspension, together with an acid substance capable of combining with the diazonium compound formed. The NO_2 ions travel towards the anode. The anode cell contains the solution or suspension, which may be neutral or alkaline, with a platinum anode. The cathode may be of any convenient metal, and is immersed in dilute sodium hydroxide, being separated from the anode cell by a diaphragm. The strength of current may vary within wide limits. Cooling is not necessary, as

the formation of the azo-compound proceeds faster than the decomposition of the diazonium salt, and the reaction is even facilitated by warming. C. H. D.

The Fluorazones, a New Group of Dyes produced from Aminoazo-dyes by Fusion with Resorcinol. LUDWIG PAUL (*Chem. Zeit.*, 1904, 28, 765—772).—The *fluorazones* are fluorescent dyes, obtained by heating aminoazo-compounds with resorcinol. *Fluorazone S* is obtained by heating benzeneazo-α-naphthylamine or *p*-sulphobenzeneazo-α-naphthylamine with resorcinol; it is insoluble in water, but dissolves in alcohol, imparting to it a violet colour; it is dichroic and shows a red fluorescence. *Fluorazone L*, which is formed with fluorazone S when *p*-sulphobenzeneazo-α-naphthylamine is heated with resorcinol, is soluble in water. Several fluorazones, for example, those obtained from Meldola's base (*p*-aminobenzeneazo-α-naphthylamine), from *p*-hydroxybenzeneazo-α-naphthylamine, and from aminoazonaphthalene, are described, but their chemical nature has not been investigated; no analyses are recorded. W. A. D.

Preparation of Polyazo-Dyes from 8-Amino-α-naphthol-3 : 6-disulphonic Acid. SCHOELLKOPF, HARTFORD & HANNA CO. (D.R.-P. 153557).—Polyazo-dyes are obtained by combining 1 mol. of a tetrazonium compound in acid solution with 1 mol. of 8-amino-α-naphthol-3 : 6-disulphonic acid. The intermediate compound thus formed is combined in alkaline or sodium acetate solution with a diazonium compound and a phenol or amine. The dyes have the constitution

$$\begin{array}{l} R^{11}N_2\cdot R\cdot N_2\cdot C{:}C(NH_2)\cdot C\cdot C(OH){:}C\cdot N_2R^1 \\ \quad SO_3Na\cdot C{=\!=\!=}CH\cdot C\cdot CH{=\!=\!=}C\cdot SO_3Na. \end{array}$$

C. H. D.

Albumins Soluble in Acetic Acid and Bence-Jones' Albumosuria. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1904, [vi], 20, 49—55. Compare Abstr., 1904, ii, 599).—It is regarded as probable, from experiments with the proteids of egg-white and serum, that between the albumins and the albumoses there exists an intermediate stage in which coagulation by heat is not easily obtained, and under the influence of weak acids, such as acetic, may be altogether absent. In two cases of Bence-Jones' albumosuria the proteid found was not a true albumose but a globulin. W. D. H.

Hydrolysis of Casein. ZDENKO H. SKRAUP (*Monatsh.*, 1904, 25, 633—656. Compare this vol., i, 538).—A detailed account of the author's method of isolating the crystalline products of the hydrolysis of casein is now given.

In addition to the products mentioned previously (*loc. cit.*), aspartic acid has been obtained.

Diaminoglutaric acid forms a *hydrochloride*, which crystallises in sheaves of needles, and a *platinichloride* and an *aurichloride* which crystallise in long, irregular needles. Aminohydroxysuccinic acid crystallises in white plates; the *copper* salt crystallises in long, blue aggregates of prisms, containing $4H_2O$, and is soluble in water.

d-Caseic acid has $[\alpha]_D + 0{\cdot}13°$; the hydrochloride crystallises in plates; the yellow *platinichloride* forms a crystalline mass; the *aurichloride* crystallises in flower-like aggregates. The inactive caseic acid forms salts identical with those from the dextrorotatory modification.

Diaminoglutaric, diaminoadipic, caseanic, and caseic acids give a yellow coloration with α-naphthol and concentrated sulphuric acid.

G. Y.

Protokyrines. MAX SIEGFRIED (*Chem. Centr.*, 1904, ii, 908; from *Ber. k. sächs. Ges. Wiss. Math. phys. Cl.*, 1904, 117—122. Compare Abstr., 1903, i, 586).—*Caseinokyrine*, prepared in a similar manner to glutokyrine, by decomposition of casein with hydrochloric acid and isolation as the sulphate, has a strong alkaline reaction and absorbs carbon dioxide from the air. The composition of the sulphate is not affected by repeated crystallisation, and the quantity of nitrogen contained in the decomposition products of each crystalline fraction was found to be the same. The sulphate has a strongly acid reaction and is readily soluble in water, but insoluble in absolute alcohol or ether. Caseinokyrine gives the biuret reaction, but the coloration is not as red as that shown by peptones which have been formed by the action of enzymes. *Caseinokyrine phosphotungstate* crystallises in groups of needle-shaped prisms. The formula of the sulphate, $C_{23}H_{47}N_9O_8,3H_2SO_4$[?], is derived from the results of analysis on the assumption that a small quantity of alcohol used in the preparation of the salt is obstinately retained. Arginine and lysine have been isolated from the decomposition products of caseinokyrine, but neither ammonia nor histidine could be detected. By the action of sulphuric acid, glutamic acid is also formed. The bases which are obtained when caseinokyrine is completely hydrolysed contain more than 80 per cent. of the nitrogen of the original kyrine.

Since histidine is formed by the complete hydrolysis of casein, but not of caseinokyrine, the histidine complex is either not present in the casein molecule (if such exists), or only in a state of feeble combination. Fibrin also yields a kyrine; the composition of the sulphate is very similar to that of caseinokyrine. E. W. W.

Oxidation of Proteids with Calcium Permanganate. I. Oxidation of Gelatin. FRIEDRICH KUTSCHER and MARTIN SCHENCK (*Ber.*, 1904, 37, 2928—2931. Compare Kutscher and Zickgraf, Abstr., 1903, i, 666).—The product obtained on oxidising a boiling solution of gelatin in water by means of calcium permanganate, after addition of ammonium carbonate and filtration, deposits white needles, apparently of oxaluramide. The filtrate deposits long needles of ammonium oxamate on evaporation. The immediate source of the ammonium oxamate must be glycine, which yields oxamic acid on oxidation with permanganates. C. H. D.

Hydrolysis of Spleen Nucleic Acid by Dilute Mineral Acid. PHOEBUS A. LEVENE (*Amer. J. Physiol.*, 1904, 12, 213—219).—When spleen nucleic acid is hydrolysed by 2 per cent. sulphuric acid at 100—125°, the main substances in solution are purine bases. The

residue resembles Neumann's nucleo-thyminic acid, and on further decomposition yields purine and pyrimidine bases; the yield of purine bases is small, and the amount of pyrimidine bases is also reduced in quantity as compared with that in the original nucleic acid. The substance which yields furfuraldehyde is almost wholly broken up by treatment with 2 per cent. sulphuric acid, and so is in loose combination in the original molecule. On the other hand, the yield of lævulic acid is so large after this treatment that a hexose or very stable polysaccharide must be in firm combination. W. D. H.

The Combination of Purine Bases in the Nucleic Acid Molecule. RICHARD BURIAN (*Zeit. physiol. Chem.*, 1904, **42**, 297—298. Compare this vol., i, 358).—Polemical against Steudel. W. D. H.

Chemical Composition of Adrenaline (Epinephrine). GABRIEL BERTRAND (*Compt. rend.*, 1904, **139**, 502—504. Compare this vol., i, 791, i, 540).—One hundred and twenty-five grams of crystallised adrenaline were obtained by working up the glands from about 4000 horses. One hundred and ten grams of this material were dissolved in acid and divided into seven fractions by successive addition of ammonia to the solution. Each of these fractions was further subjected to similar treatment. The analyses of the products obtained at different stages are very concordant and indicate the purity of the original adrenaline, the composition of which is represented by $C_9H_{13}O_3N$. For the molecular weight in acetic acid, 174·3 was obtained (theory 183) (compare Jowett, Trans., 1904, **85**, 192). H. M. D.

Studies on Enzyme Action II. Rate of the Change conditioned by Sucroclastic Enzymes, and its Bearing on the Law of Mass Action. E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1904, **73**, 500—516. Compare Trans., 1903, **83**, 1305).—The author has studied the action of lactase and emulsin on milk sugar, and of maltase on maltose, and the results obtained, taken in conjunction with those of earlier workers (Adrian Brown, Trans., 1902, **81**, 373; Horace Brown and Glendinning, *ibid.*, 388), strongly support the view that the rate of change is essentially dependent on the relative proportions of enzyme and sugar. On the hypothesis that the enzyme combines with the sugar, the effects of varying the conditions may be predicted as follows in harmony with the observed facts: (1) if the amount of enzyme is small, relatively to the initial amount of sugar, the change is at first a linear function of the time; as hydrolysis proceeds, and the amount of enzyme is relatively greater, the change is approximately a logarithmic function of the time, as required by the law of mass action. (2) If the amount of enzyme is initially considerable compared with the amount of sugar, the linear part of the change is not apparent. (3) When the amount of enzyme decreases during hydrolysis, owing to the influence of the products, the rate of change will be governed by an equation of the second order, so that the values of the velocity constant K, calculated for the simple logarithmic formula, will gradually diminish. (4) If the amounts of enzyme and

water are kept constant, an increase in the amount of sugar beyond that required for complete combination with the enzyme will not augment the quantity of hydrolyte undergoing change in a given time. The proportion of the hydrolyte changed, and the value of K, will, however, decrease as the sugar concentration is increased.

J. C. P.

Studies on Enzyme Action. III. Influence of the Products of Change on the Rate of Change conditioned by Sucroclastic Enzymes. E. Frankland Armstrong (*Proc. Roy. Soc.*, 1904, 73, 516—526. Compare preceding abstract).—In the previous paper, retardation of the hydrolysis of a sugar was attributed to the influence of the products of change on the enzyme. The extent of this influence has been studied, and it is found that in the hydrolysis of lactose by lactase, retardation is due to galactose, whilst dextrose and lævulose are almost without influence. The hydrolysis of lactose by emulsin is considerably retarded by dextrose, slightly by galactose, and not perceptibly by lævulose. The relative effect of dextrose, galactose, and lævulose on the hydrolysis of maltose by maltase is the same as that just mentioned. Hydrolysis by invertase, on the other hand, is retarded by lævulose, but not by dextrose. When Fischer's observations are taken into account, it is seen that the only hexoses which retard hydrolysis by any given enzyme are those derived from the hexosides which that enzyme can hydrolyse. This result is proof of the closely-related configurations of enzyme and hydrolyte, and may be taken as evidence that the enzyme combines with the hexose in such a way that it is withdrawn from the sphere of action.

It is noteworthy that the action of emulsin on lactose is retarded not only by dextrose, but also, although to a less extent, by α methylglucoside, which is not itself attacked by emulsin. So also α-methylgalactoside, although unaffected by the enzyme, retards the hydrolysis of lactose by lactase just as much as galactose itself. On the other hand, α-methylglucoside, like dextrose, has no retarding influence on the hydrolysis of lactose by lactase. Further, the action of maltase on maltose is retarded by β-methylglucoside, which is unaffected by that enzyme. Consideration of these and other facts leads to the view that enzyme and hydrolyte must be in complete correlation, and are probably attached along the line of carbon atoms. J. C. P.

Studies on Enzyme Action. IV. Sucroclastic Action of Acids as contrasted with that of Enzymes. E. Frankland Armstrong and Robert John Caldwell (*Proc. Roy. Soc.*, 1904, 73, 526—537. Compare preceding abstracts).—The results of the experiments described in this paper are summarised as follows. The hydrolysis of lactose in presence of hydrochloric acid takes place in accordance with the logarithmic law, although in concentrated solutions there is a marked tendency for reversion to take place, with the result that the course of change in its later stages departs from the said law. The rate of hydrolysis for lactose is remarkably slow compared with that for sucrose, but the effect of increasing the concentration resembles that produced by changes of concentration in the case of sucrose and

maltose. The products of hydrolysis exert an influence on the rate of change comparable with that exercised by lactose itself. Rise of temperature has even more influence on the rate of hydrolysis of lactose than on that of sucrose.

So far as the theory of hydrolysis by acids is concerned, the authors take a view similar to that adopted in the case of enzyme action. It is supposed that an active system is formed by a combination of a part of the sugar with a part of the acid, and that at a given temperature there will be an equilibrium between water, sugar, and acid. This view of hydrolysis as depending on association affords an explanation of the great influence of temperature-changes on the rate of hydrolysis. Emphasis is laid also on the differences in the behaviour of enzymes and acids as hydrolytic agents. The two important points in this connection are (1) the superior affinity of the enzymes for the carbohydrates; (2) the very different behaviour of enzymes and acids towards water—a consequence of the colloid nature of the former and the crystalloid nature of the latter.

J. C. P.

Enzyme Action as bearing on the Validity of the Ionic Dissociation Hypothesis and on the Phenomena of Vital Change. Henry E. Armstrong (*Proc. Roy. Soc.*, 1904, **73**, 537—542).—The selective character of the influence exerted by enzymes (see previous abstracts) is regarded as final proof that the action depends not on dissociation, but on association. This view is held also with regard to the hydrolysis of sugars by acids and chemical change generally.

The conception of the enzyme as associated at several points with the carbohydrate molecule is discussed in relation to fermentative changes, and it is further thought probable that this conception will furnish an interpretation of many hitherto unexplained phenomena.

J. C. P.

Lability of Enzymes. Keijirō Asō (*Bul. Coll. Agric. Tōkyō.* 1904, **6**, 57—75).—Small amounts of dicyanogen do not destroy enzymes in a very diluted condition. Nitrous acid is more injurious than equally diluted nitric acid.

Enzymes are destroyed by dilute neutral solutions of hydrazine, methylhydrazine, and hydroxylamine. This would accord with the assumption that the active grouping in the enzymes is ketonic (Loew) or aldehydic.

N. H. J. M.

Action of Hydrogen Peroxide on Enzymes. Alb. J. J. Vandevelde (*Beitr. chem. Physiol. Path.*, 1904, **5**, 558—570).—Hydrogen peroxide favours the action of rennin, pepsin, trypsin, and the proteolytic enzyme of milk. It has no such action on katalase or on diastatic ferments; these it inhibits. This difference is explicable on Loew's "lability hypothesis."

W. D. H.

Invertase from Yeast. B. Hafner (*Zeit. physiol. Chem.*, 1904, **42**, 1—34).—Invertase has been obtained by Osborne's method

(Abstr., 1899, i, 967) from a pure press yeast and also from a "bottom" beer yeast. The amount of invertase in the former case was small; it contains, however, only a small amount of ash (2—4 per cent.), and different specimens vary but little in composition. The yield from the "bottom" yeast is much better, but the product is not so pure. It has been found that the invertase from press yeast is far more sensitive to the action of alcohol or ammonia than that obtained from bottom yeast.

It has not been found possible to remove the phosphoric acid entirely from yeast either by precipitation as magnesium ammonium phosphate or by prolonged dialysis. The conclusion is drawn that a considerable amount of the phosphoric acid is in a state of combination in the diastase molecule. This is confirmed by an examination of the ash, which contains a much larger amount of phosphoric acid than could be combined with the bases present in the ash.

It has also not been found possible to obtain an active diastase preparation free from carbohydrate. When the preparation is subjected to prolonged dialysis, considerable amounts of the active ferment and of the carbohydrate pass through the membrane, and the solution left in the inner vessel is not free from carbohydrate. It is thought probable that part, at any rate, of such carbohydrate forms an integral part of the diastase molecule.

The nitrogen contained in the diastase molecule does not form part of a complex nitrogenous group such as albumose, peptone, &c., since (1) preparations of the ferment do not lose their activity when subjected to prolonged treatment with trypsin solution and (2) diastase does not give the biuret reaction.

An apparatus is described for keeping the inner and outer liquids in motion during dialysis. J. J. S.

Yeast Catalase. WLADIMIR ISSAEW (*Zeit. physiol. Chem.*, 1904, **42**, 102—116. Compare Loew, Abstr., 1901, i, 435; 1903, i, 544; Senter, *ibid.*, 1903, ii, 661, and Neumann-Wender, this vol., i, 542).—The greater part of yeast catalase is precipitated when yeast extracts are mixed with their own weight of alcohol, and the activity is not increased by redissolving and precipitating a second time. The activity of the solutions appears to reach its maximum at 40°; it is less at 0° and at 50° and is completely destroyed by boiling for 15 minutes. The decomposition of hydrogen peroxide by the catalase is a true enzymatic reaction and at any time is proportional to the concentration of the peroxide provided the concentration is not too great. In this case, probably, secondary reactions such as the oxidation of the catalase occur. The amount of decomposition is not directly proportional to the amount of enzyme, and when the amount of enzyme is considerable the reaction appears to be no longer unimolecular. When subjected to dialysis, the enzyme becomes less active. The presence of small amounts of potassium dihydrogen phosphate appears to favour the decomposition, but even small amounts of sulphuric acid have an unfavourable effect. J. J. S.

Yeast Oxydase. WLADIMIR ISSAEW (*Zeit. physiol. Chem.*, 1904, **42**, 132—140. Compare Grüss, Abstr., 1901, ii, 615).—An oxydase has

been extracted from yeast by the aid of water or glycerol, and its action at constant temperature on various substances studied. It can not merely oxidise the reducing substances present in the yeast extract, but, if these are previously oxidised by passing air through the solution, it will then oxidise other substances, such as quinol, pyrogallol, &c. The amount of oxydase is often small, and on this account it is sometimes difficult to obtain good oxidation phenomena. Top yeasts appear to contain more than bottom yeasts. J. J. S.

The Activity of Zymase and of Endotryptase in Dead Yeast Cells under Varying Conditions. T. Gromoff and O. Grigorieff (*Zeit. physiol. Chem.*, 1904, 42, 299—329).—Commercial zymin contains a strong proteolytic enzyme (E. Buchner's endotryptase), the activity of which is largely destroyed by the presence of sucrose, dextrose, lactose, mannitol, alcohol, quinine, glycine, or glycerol. In the case of sucrose, the retardation appears to be proportional to the concentration.

When isotonic solutions of different substances are employed, the retardations are very different, being greatest with sucrose and least with glycine. This can be explained by supposing that with certain reagents, for example, sucrose, proteid synthesis as well as proteolysis occurs. The products of decomposition also appear to retard proteolysis. Certain mineral salts such as calcium chloride or potassium nitrate in dilute solutions accelerate the decomposition either alone or in the presence of sucrose or dextrose.

Experiments have been conducted on the activity of zymase contained in commercial zymin mainly in the form of roll (cylinder) cultures. The amount of carbon dioxide evolved depends largely on the nature of the culture medium; if this contains fermentable substances, the amount of carbon dioxide evolved per hour is greater than when only non-fermentable substances (mannitol or lactose) are present. In the latter case, the amount of carbon dioxide evolved is exactly the same as in self-fermentation. The amount of carbon dioxide evolved per hour gradually decreases, and finally becomes nil owing to the destruction of the zymase by the endotryptase. The addition of fresh zymin again induces evolution of carbon dioxide, but in increased quantity, indicating that the products of fermentation accelerate the decomposition; this is confirmed by the fact that the amounts of carbon dioxide evolved by 1 and 2 grams respectively of zymin are in the ratio 1 : 3.

No differences can be detected when the experiments are conducted in oxygen or in hydrogen. The concentration of the sucrose does not affect the amount of carbon dioxide, but poisonous substances (alcohol, quinine) and salt solutions (calcium chloride and potassium nitrate) have exactly opposite effects to those described in the case of the proteolytic enzyme. J. J. S.

Organic Chemistry.

Oxidation of Methyl and Ethyl Alcohols at their Boiling Points René Duchemin and Jacques Dourlen (*Compt. rend.*, 1904, **139** 679—681).—The authors find that when methyl or ethyl alcohol is distilled in a reflux apparatus, either alone or in the presence of copper, lead, tin, or zinc shot, it is oxidised to formic or acetic acid respectively, the quantity of the acid increasing with the duration of the distillation and varying with the nature of the metal employed, being greatest in the case of copper. In the experiments described, the free acid was titrated with $N/100$ sodium hydroxide in the presence of phenolphthalein, correction being made for the initial acidity of the alcohol employed. The formation of acetic acid from alcohol in these circumstances is probably due to the dehydrogenation of the alcohol in the presence of the metal to form the metallic hydride and aldehyde; the former is broken down into its elements as the reaction proceeds, and the latter is oxidised to acetic acid by the oxygen dissolved in the alcohol. The oxidation of alcohol in the presence of metals has already been investigated by Sabatier and Senderens (compare Abstr., 1903, i, 393, 453) and by Trillat (compare Abstr., 1903, i, 222; ii, 589). M. A. W.

Action of Magnesium Methyl Iodide on Mesityl Oxide and Phorone. Th. von Fellenberg (*Ber.*, 1904, **37**, 3578—3581).—Magnesium alkyl haloids react with $\alpha\beta$-unsaturated ketones, yielding doubly unsaturated hydrocarbons, the tertiary alcohols at first formed being unstable (Grignard, Abstr., 1900, i, 382). In the case of mesityl oxide and phorone, it is possible to isolate the alcohols.

β-Hydroxy-βδ-dimethyl-γ-pentene, $CMe_2:CH\cdot CMe_2\cdot OH$, prepared from mesityl oxide and magnesium methyl iodide, forms a colourless, aromatic liquid, boiling at 46° under 14 mm. pressure and having a sp. gr. 0.8397 at 22·5°/4°, $\mu = 1{\cdot}44009$ at 22·5°, and a molecular refraction 35·815. When distilled under the ordinary pressure or with sodium, water is removed and βδ-dimethyl-αγ-pentadiene is obtained.

δ-Hydroxy-βδζ-trimethyl-βε-heptadiene,

$$CMe_2:CH\cdot CMe(OH)\cdot CH:CMe_2,$$

from phorone and magnesium methyl iodide, forms white needles melting at 57·5° and boiling at 43—46° under 0·25 mm. pressure. It is without odour when solid, but has an intense camphor-like odour when fused. The alcohol rapidly absorbs oxygen, forming a syrupy compound, $C_{10}H_{18}O_3$, with an odour of peppermint.

When distilled from sodium under 14 mm. pressure, the alcohol passes into *trimethylheptatriene* [*βζ-dimethyl-δ-methylene-βε-heptadiene*], $CMe_2:CH\cdot C(CH_2)\cdot CH:CMe_2$, boiling at 55—57°. C. H. D.

Action of Hydrogen Chloride on Aqueous Formaldehyde and Trioxymethylene. Franz M. Litterscheid and K. Thimme (*Annalen*, 1904, 334, 1—49).—The investigations hitherto made on the action of hydrogen chloride on formaldehyde are contradictory, and have been repeated and amplified in this communication.

When hydrogen chloride is passed into a solution of commercial formalin containing methyl alcohol, chloromethyl ether, dichloromethyl ether, dichlorotrioxymethylene, and dichlorotetraoxymethylene are produced (compare Litterscheid, Abstr., 1901, i, 443; and Sonay, *Bull. Acad. roy. Belg.*, 1894, 28, 629). The four substances can be isolated and recognised by the aid of their trimethylamine additive products.

In the absence of methyl alcohol, dichloromethyl ether and dichlorotrioxymethylene, together with dichlorotetraoxymethylene, are formed. It is also shown that, in the action of hydrogen chloride on commercial formalin or pure formaldehyde solution, the compounds obtained by Lösekann (Abstr., 1892, 423) and Coops (Abstr., 1902, i, 77), chloromethyl alcohol, hydroxychloromethyl ether, and hydroxychlorotrioxymethylene, do not appear to exist. Similarly, the chloromethyl alcohol of Grassi-Cristaldi and Maselli (Abstr., 1898, i, 294) is dichlorotrioxymethylene.

The formaldehyde solution used contained 37·1 per cent. of formaldehyde and a small quantity of acetone. The methyl alcohol was estimated by treating the solution with $1\frac{1}{2}$ volumes of 10 per cent. ammonia, then acidifying and distilling, and determining the sp. gr. of the distillate; it amounted in this specimen to 12 per cent., in the "Formal I" of the Farbwerke vorm. Meister, Lucius, & Brüning to 18 per cent., and in another commercial preparation to 11 per cent.

The commercial formalin was saturated at 0° with dry hydrogen chloride, when an oily liquid separated; after repeated fractionation, this liquid was divided into four fractions: a large fraction, *A*, boiling at 58·5—62°; a small fraction, *B*, boiling at 70—100°; a second large fraction, *E*, boiling at 100·5—101·5°; and another small fraction, *D*, boiling at 91—92°. These fractions were treated in ethereal solution with trimethylamine and the resulting additive products studied in the form of their platinum and gold salts.

Fraction *A* consisted only of chloromethyl ether; the *additive* product with trimethylamine, $OMe{\cdot}CH_2,NMe_3Cl$, forms crystals, and the *platinichloride*, $(OMe{\cdot}CH_2,NMe_3Cl)_2,PtCl_4$, crystallises in brownish-red prisms melting at 228—229°. Fraction *B* is a mixture of chloro- and dichloro-methyl ether. The *additive* product with trimethylamine is treated in aqueous solution with platinic chloride, when the *platinichloride* of the dichloro-compound, $O(CH_2{\cdot}NMe_3Cl)_2,PtCl_4,H_2O$, crystallises in four-sided leaflets melting at 241°; the *platinichloride* of the monochloro-compound remains in the mother liquor. Fraction *D* also contains these two compounds. Fraction *E* consists only of dichloromethyl ether.

The residue boiling above 103° was fractionated and yielded: fraction *F*, which contained, besides dichloromethyl ether, dichlorotrioxymethylene, the trimethylamine *additive* product of which yields a *platinichoride*, $(NMe_3Cl{\cdot}CH_2{\cdot}O)_2CH_2,PtCl_4$, which forms rhombic crys-

tals melting at 235—240°. Fraction *G*, boiling above 117°, contained mainly dichlorotetraoxymethylene, the trimethylamine additive product of which yielded a *platinichloride*, $(NMe_3Cl\cdot CH_2\cdot O\cdot CH_2)_2O,PtCl_4$, a pale yellow precipitate. Dichloromethyl ether and dichlorotrioxymethylene were also probably present in this fraction. Fraction *H*, boiling above 125°, consists mainly of dichlorotetraoxymethylene, the trimethylamine *additive* product of which yields an *aurichloride*, $(NMe_3Cl\cdot CH_2\cdot O\cdot CH_2)_2O,2AuCl_3$, melting at 204°. It is claimed that these results show that Coops' observations (*loc. cit.*) are incorrect.

A solution of formaldehyde free from methyl alcohol was obtained by distilling trioxymethylene in a copper retort and collecting the distillate in water. The product of the action of hydrogen chloride on this solution was treated in the same manner as above described. Dichloromethyl ether, dichlorotrioxymethylene, and dichlorotetraoxymethylene were isolated. The dichlorotrioxymethylene is identical with Sonay's dichloromethylal, which was obtained by chlorinating methylal. The additive compound of the trioxymethylene with pyridine was prepared from the substance obtained from both sources and converted into a *platinichloride*, $(C_5NH_5Cl\cdot CH_2\cdot O)_2CH_2,PtCl_4$, which crystallised in plates, and an *aurichloride*,

$$(C_5NH_5Cl\cdot CH_2\cdot O)_2CH_2,2AuCl_3,$$

crystallising in needles.

A repetition of Grassi-Cristaldi and Maselli's experiments on the action of hydrogen chloride on trioxymethylene at 180°, in which they stated chloromethyl alcohol was formed, showed that only dichloromethyl ether and dichlorotrioxymethylene were produced.

Determinations of the molecular weight of formaldehyde in dilute aqueous solution showed that formaldehyde was partly present in a polymeric form, probably trioxymethylene, a result previously obtained by Tollens and Kraut for more concentrated solutions.

K. J. P. O.

Reactions of Chloromethyl Alkyl Ethers. FRANZ M. LITTERSCHEID and K. THIMME (*Annalen*, 1904, 334, 49—67. Compare preceding abstract).—As a means of recognising and isolating the substituted methyl ethers described in the preceding abstract, the reaction of these compounds with organic bases has been investigated.

Chloromethyl ether is best prepared by treating trioxymethylene with methyl-alcoholic hydrogen chloride and then passing in hydrogen chloride until solution is complete; the ether is then rectified. The *picrate*, $OMe\cdot CH_2\cdot NMe_3\cdot O\cdot C_6H_2(NO_2)_3$, crystallises in dark yellow needles melting at 198°. The ether unites with pyridine in ethereal solution, the *additive* product forming a *mercurichloride*,

$$C_5NH_5Cl\cdot CH_2\cdot OMe,HgCl_2,$$

which crystallises in four-sided plates melting at 91°. In the absence of a diluent, pyridine decomposes the chloro-ether, pyridine hydrochloride being formed. Chloromethyl ether and quinoline yield an *additive* product in the presence of chloroform, the *platinichloride* of which, $(C_9NH_7Cl\cdot CH_2\cdot OMe)_2,PtCl_4$, crystallises in rhombic plates melting at 232—234°; the *aurichloride*, $C_9NH_7Cl\cdot CH_2\cdot OMe,AuCl_3$, forms

golden-yellow, rhombic plates melting at 126—127°. The *additive* compound with strychnine, $C_{21}H_{22}O_2N_2,CH_2Cl\cdot OMe$, forms leaflets; its *platinichloride*, $(C_{21}H_{22}O_2N_2,CH_2Cl\cdot OMe)_2,PtCl_4$, forms brown crystals which do not melt at 250°; the *aurichloride*,

$$C_{21}H_{22}O_2N_2,CH_2Cl\cdot OMe,AuCl_3,$$

crystallises in needles melting at 193°. The *additive* compound with narcotine, $C_{22}H_{23}O_7N,CH_2Cl\cdot OMe$, crystallises in leaflets melting and decomposing at 210° and is decomposed on treatment with gold chloride. The *additive* compound with hexamethylenetetramine, $C_6H_{12}N_4,CH_2Cl\cdot OMe$, is decomposed by gold chloride, the *aurichloride* of hexamethylenetetramine, $C_6H_{12}N_4,HAuCl_4$, being formed and crystallising in golden-yellow needles melting at 192°. The *additive* compound with cytisine was only isolated in the form of the gold *salt*, $C_{11}H_{14}ON_2,CH_2Cl\cdot OMe,AuCl_3$, which forms crystals melting and decomposing at 202°. The *additive* product with dimethylamine is hygroscopic and yields an *aurichloride*, $NMe_2Cl(CH_2\cdot OMe)_2,AuCl_3$, which crystallises in leaflets melting at 86—88°, and is not a simple additive product, but a quaternary base. The *platinichloride*, $[NMe_2Cl(CH_2\cdot OMe)_2]_2,PtCl_4$, is obtained from the aurichloride and crystallises in rhombic plates melting at 197°. If the aqueous solution of the additive product is directly treated with platinic chloride, a mixture of substances is produced; one *compound*,

$$NMe_2Cl(CH_2\cdot OMe)_2,3[(NHMe_2)_2,2HPtCl_5],$$

crystallises in rosettes melting at 212—214°; another compound, $NMe_2Cl(CH_2\cdot OMe)_2,PtCl_4,2[(NHMe_2)_2,H_2PtCl_6]$, crystallises in needles melting at 202—204°.

Chloromethyl ether forms both with phenol and aniline amorphous insoluble condensation products.

Chloromethyl ethyl ether forms with trimethylamine a crystalline additive product, $NMe_3Cl\cdot CH_2\cdot OEt$; the *platinichloride*,

$$(NMe_2Cl\cdot CH_2\cdot OEt)_2,PtCl_4,(NHMe_3Cl)_2,PtCl_4,$$

is a yellow salt melting at 226°. The *aurichloride*,

$$NMe_3Cl\cdot CH_2\cdot OEt,AuCl_3,$$

crystallises in leaflets melting at 139°. The normal *platinichloride*, $(NMe_3Cl\cdot CH_2\cdot OEt)_2,PtCl_4$, can be prepared from the aurichloride and crystallises in leaflets melting at 230°. The *additive* product with pyridine, $C_5NH_5Cl\cdot CH_2\cdot OEt$, yields a *platinichloride*,

$$(C_5NH_5Cl\cdot CH_2\cdot OEt)_2,PtCl_4,$$

crystallising in plates which melt at 178°; the *aurichloride*, $C_5NH_5Cl\cdot CH_2\cdot OEt,AuCl_3$, crystallises in leaflets melting at 87—88°.

Dichloromethyl ether forms an *additive* product with quinoline, $(C_9NH_7,CH_2Cl)_2O$, which yields a *platinichloride*,

$$(C_9NH_7,CH_2Cl)_2O,PtCl_4,$$

crystallising in needles melting at 232°; the *aurichloride*, $(C_9NH_7,CH_2Cl)_2O,AuCl_3$, crystallises in needles which do not melt at 250°. The additive compounds of this ether are more stable than those of chloromethyl ether. K. J. P. O.

Action of Methyl Sulphate on Sodium Hyposulphite. ARTHUR BINZ (*Ber.*, 1904, 37, 3549—3550. Compare Bernthsen and

Bazlen, Abstr., 1900, ii, 203).—*Methyl sodium thiosulphate* is formed when methyl sulphate and sodium hyposulphite are warmed together for a few minutes at 70° and the product extracted with boiling alcohol. If the heating is continued at 70° or at a higher temperature in a reflux apparatus, sulphur dioxide, methyl sulphide, and methyl disulphide are evolved, and on heating to 200° a sublimate of dimethylsulphone is formed. G. Y.

Electrolysis of Potassium Acetate. FRITZ FOERSTER and A. PIGUET (*Zeit. Elektrochem.*, 1904, 10, 729—736).—When an aqueous solution of potassium acetate is electrolysed with a smooth platinum anode, the principal reaction is $2KC_2H_3O_2 + 2H_2O = H_2 + 2KOH + C_2H_6 + 2CO_2(1)$. In addition to this, acetic acid may be oxidised to carbon dioxide or to carbon monoxide, $CH_3{\cdot}CO_2H + 4O = 2CO_2 + 2H_2O(2)$ and $CH_3{\cdot}CO_2H + 2O = 2CO + 2H_2O(3)$, or free oxygen may be formed. The authors find that an iridium anode gives the same products as one of smooth platinum. With platinised platinum, carbon dioxide and oxygen are the main products; a little carbon monoxide is also formed, but no ethane, unless the anode has first been anodically polarised in a solution of sodium hydroxide. Iron and palladium behave in the same way as unpolarised platinised platinum. It appears that the different behaviour of the metals is connected with the varying potentials at which oxygen is liberated at them, the potential required for the formation of ethane lying below that at which oxygen is evolved at platinum or iridium anodes, but above the value for iron or palladium anodes.

The variations of *E.M.F.* observed during the electrolysis are also discussed at some length, but no definite result is arrived at.

T. E.

Measurements of Conductivity of Unsaturated Acid. FRITZ FICHTER and ALFRED PFISTER (*Annalen*, 1904, 334, 201—210).—Redetermination of the dissociation-constant of vinylacetic acid has shown that the number previously recorded (Abstr., 1902, i, 256) is erroneous, and that the mean value of K is 0·00383. This number is twice as large as that observed by Ostwald for crotonic acid, $K = 0{\cdot}00204$. This is the first recorded instance of a pair of unsaturated acids differing only in the position of the double linking, in which the $\beta\gamma$-unsaturated acid possesses a higher degree of dissociation than the $\alpha\beta$-acid. A series of unsaturated isomeric acids, differing only in the position of the double linking, have been investigated, and it has been demonstrated that the dissociation constant of the $\beta\gamma$-acid always is distinctly higher than that of the $\alpha\beta$-acid. This rule holds both for aliphatic and cyclic compounds, and is solely dependent on the relative positions of the double linking and the carboxyl group. If the double linking is in the $\gamma\delta$- or in the $\delta\epsilon$-positions relative to the carboxyl group, there appears to be a regular decrease of the dissociation coefficient.

The following table gives a summary of the results :

Butyric acid	0·00154	Valeric acid	0·00161
Crotonic acid	0·00204	$\alpha\beta$-Pentenoic acid	0·00148
Vinylacetic acid	0·00383	$\beta\gamma$-Pentenoic acid	0·00335
		$\gamma\delta$-Pentenoic acid	0·00209
α-Methyl-$\alpha\beta$-pentenoic acid	0·00097	Hexoic acid	0·00146
α-Methyl-$\beta\gamma$-pentenoic acid	0·00299	$\alpha\beta$-Hexenoic acid	0·00189
α-Methyl-$\gamma\delta$-pentenoic acid	0·00216	$\beta\gamma$Hexenoic acid	0·00264
		$\gamma\delta$-Hexenoic acid	0·00174
		$\delta\epsilon$-Hexenoic acid	0·00191

From these results, it follows that the $\alpha\beta$-unsaturated acids are feebler acids than would be expected from the negative character of the double linking and the greater influence of α-substituents on the affinity constants of acids. This fact is accounted for, by the help of Thiele's theory of partial valencies. In the case of the $\alpha\beta$-unsaturated acids, a conjugated system of double linkings is present, and as a consequence the system is less unsaturated than in the case of the $\beta\gamma$- or $\gamma\delta$ unsaturated acids, thus: $C{\cdot}C{:}C{\cdot}C{:}O$ and $C{:}C{\cdot}C{\cdot}C{:}O$.

K. J. P. O.

Acetyl Derivative of Fermentation Lactic Acid. Richard Anschütz and W. Bertram (*Ber.*, 1904, 37, 3971—3974).—Acetyl-*i*-lactic acid, $OAc{\cdot}CHMe{\cdot}CO_2H$, prepared by the action of acetyl chloride on *i*-lactic acid, melts indefinitely at 57—60°, boils at 127° under 11 mm. pressure, and is deliquescent. The action of water on it at various temperatures was investigated; at the ordinary temperature it is slowly hydrolysed, whilst at 150—160° for five hours it is completely hydrolysed. *Acetyl-lactyl chloride* boils at 56° under 11 mm. pressure and at 150° under 760 mm. pressure. It has sp. gr. 1·1920 at 17°/4° and n_D 1·4241 at 17°.

Guaiacol acetyl-lactate, $OAc{\cdot}CHMe{\cdot}CO_2{\cdot}C_6H_4{\cdot}OMe$, prepared by heating acetyl-lactic acid chloride with guaiacol until the evolution of hydrogen chloride ceases, melts at 71° and boils at 180° under 13 mm. pressure. It separates from ether, chloroform, or benzene in pyramids.

Acetyl-lactylanilide, prepared by the action of acetyl-lactic acid chloride on an ethereal solution of aniline, separates from dilute alcohol in silky needles and melts at 121—122°.

Acetyl-lactylphenetidide separates from water in glistening needles and melts at 129°.

Acetyl-lactonitrile, prepared by the action of acetyl chloride on lactonitrile, boils at 73° under 8 mm. pressure and at 172—173° under 760 mm. pressure.

A. McK.

Lactonic Acids, Lactones, and Unsaturated Acids. Rudolf Fittig (*Annalen*, 1904, 334, 68—143).—In this paper, a number of observations are collected which complete and amplify the researches already carried out in this field.

I. *Isomeric Hydroxyvalerolactones.*—[With ERICH LEPÈRE.]—In the transformation of α-hydroxy-acids into α- and γ-ketonic acids, hydroxy-lactones are supposed to be formed as intermediate products; thus a hydroxyvalerolactone is formed in the transformation of α-hydroxy-pentenoic acid. The constitution of this lactone is uncertain, and has consequently been reinvestigated.

α-Hydroxyvalerolactone is synthesised by preparing the nitrile, $OH\cdot CHMe\cdot CH_2\cdot CH(OH)\cdot CN$, by adding molecular quantities of potassium cyanide and hydrochloric acid to an ethereal solution of freshly distilled aldol cooled to $-10°$; the nitrile is obtained as an oil contaminated with small quantities of the aldol, and *iso*dialdan (m. p. 113—114°). The crude nitrile was converted by treatment with concentrated hydrochloric acid in ethereal solution into the *lactone*, which was purified by means of the calcium salt of the dihydroxyvaleric acid, and forms a colourless neutral liquid. *Calcium α-dihydroxyvalerate*, $(C_5H_9O_4)_2Ca$, and the *barium* salt are amorphous, hygroscopic powders; the *zinc* salt crystallises in prisms.

When the calcium salt of $\alpha\gamma$-hydroxyvaleric acid is boiled with dilute hydrochloric acid, a lactone, iso*hydroxyvalerolactone*, isomeric with α-hydroxyvalerolactone, is formed; it can readily be separated from the α-compound by conversion into the calcium salt of the dihydroxy-acid, which differs from the calcium salt of the $\alpha\gamma$-dihydroxy-acid corresponding with the α-hydroxylactone by being insoluble in alcohol. After five hours' boiling, 50 per cent. of the α-lactone is converted into the new compound. The latter is a thick, colourless oil. The *calcium* salt forms crystals, the *barium* salt crystallises with H_2O in needles or plates, and the *silver* salt crystallises in needles which are converted into leaflets by rubbing. The *iso*hydroxyvalerolactone cannot be reconverted into the α-hydroxy-compound; when the calcium salt is boiled with hydrochloric acid, lævulic acid is alone produced.

The third hydroxyvalerolactone, the α-hydroxyvalerolactone prepared from α-hydroxypentenoic acid, is not identical with the α-hydroxy-valerolactone obtained from aldolcyanohydrin, since the calcium salt does not yield *iso*hydroxyvalerolactone when boiled with hydrochloric acid, but is converted into lævulic acid. The three hydroxyvalerolactones distil undecomposed; α-hydroxyvalerolactone boils at 245—260°, *iso*hydroxyvalerolactone at 250—255°, and the hydroxy-valerolactone from the pentenoic acid at 240—260°. None of the compounds are volatile with water vapour.

It is suggested that in the conversion of the α-hydroxyvalerolactone into the *iso*-compound the hydroxy-group migrates from the α- to the β-position. It is probable that the *iso*lactone and the lactone from the hydroxypentenoic acid are stereoisomeric.

II. *Isomeric Ethyl Crotonates.*—[With PERCY BORSTELMANN and MARK LURIE.]—When diethylglycollic acid (α-hydroxy-α-ethylbutyric acid), which is, contrary to expectation, volatile with steam, is distilled, two fractions are obtained, boiling at 150° and above 200°. Two isomeric acids can be isolated from the product by neutralising with calcium carbonate and evaporating until needles crystallise out. The crystals are more soluble in cold water than in hot; from the hot solution, which has been filtered from the one calcium salt, the other

calcium salt separates. The calcium salt, which is less soluble in hot water, is the salt of *α-ethyl*iso*crotonic acid*, $CHMe{:}CEt{\cdot}CO_2H$, which is an oily liquid, boiling at 199·5° under 750 mm. pressure and not solidifying at −19°; the *calcium* salt crystallises with $2H_2O$ in needles. The more soluble *calcium* salt, $(C_6H_9O_2)_2Ca,5H_2O$, is the salt of the solid ethylcrotonic acid, isomeric with the acid just mentioned.

When the *iso*-acid is boiled for several hours, it is converted completely into the isomeride. On oxidising the calcium salt with permanganate at 0°, oxalic acid and a dihydroxy-acid, $C_6H_{12}O_4$, are produced; the latter is called iso*hexeric acid*, and is identical with the acid previously described by Fittig and Howe (Abstr., 1880, 376) as hexeric acid, the name hexeric acid being now reserved for the product of oxidation of ethylcrotonic acid; it melts at 144·5—145°, and is not volatile with steam; its *calcium* salt crystallises with $2H_2O$.

It is thought that the ethyl*iso*crotonic acid bears the same relation to ethylcrotonic acid as angelic does to tiglic acid; the calcium salts show the same differences in their solubilities, and the boiling points bear the same relation. Their behaviour towards bromine is different; whilst both angelic and tiglic acids yield the same product, dibromotiglic acid, the ethylcrotonic acids give two different compounds. The *dibromide* of ethyl*iso*crotonic acid, prepared by the action of bromine in chloroform solution in diffused daylight, forms colourless, monosymmetric crystals melting at 116·5°, and is decomposed by boiling with water or aqueous sodium carbonate into bromoamylené and *iso*hexeric acid; the *dibromide* of ethylcrotonic acid (m. p. 83·5°) also yields *iso*hexeric acid on heating with water. It is probable that the production of the same acid is accounted for by a transformation of the dibromoethylcrotonic acid.

β-Hydroxy-*α*-ethylbutyric acid, which is prepared by reduction of ethyl acetoacetate in aqueous alcoholic solution by 4 per cent. sodium amalgam and purified by means of the zinc salt, yields on distillation the same products as the *α*-hydroxy-acid. The *calcium* and *barium* salts are anhydrous and amorphous, the *zinc* salt crystallises with H_2O.

III. *Polymerisation of Phenyl*iso*crotonic Acid.*—[With Karl Hadorff.] (Compare Abstr., 1898, i, 196.)—In continuation of previous work (*loc. cit.*), the behaviour of phenyl*iso*crotonic acid towards hydrochloric acid of different concentrations has been tested. When heated with a mixture of one volume of concentrated hydrochloric acid and three volumes of water, phenylbutyrolactone is alone formed, but with a mixture of hydrochloric acid (1 vol.) and water (2 vols.) a small quantity of a new acid is also produced, the amount of which increases as the concentration of the hydrochloric acid increases. This new acid is formed without disturbing the equilibrium between the *iso*crotonic acid and the lactone, the reaction coming to an end when 65 per cent. of the acid has changed. The acid, which is now called diphenyloctolactonic acid, is identical with the polymeric phenyl*iso*crotonic acid previously described (Abstr., 1885, 528; 1890, 894), and probably has the constitution

$$CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CHPh{\cdot}CH{<}\begin{matrix}CHPh{\cdot}O\\ | \\ CH_2{-\!-}CO\end{matrix};$$

it is a monobasic acid crystallising in leaflets melting at 179°, and

yields two series of salts, in one of which the lactone ring is broken. The *calcium* salt of the lactone, $(C_{20}H_{19}O_4)_2Ca$, is crystalline, but the *barium* and *silver* salts amorphous; the *barium* and *silver* salts of the dibasic hydroxy-acid were prepared.

When oxidised with chromic acid, benzoic acid is produced together with diphenylketo-octonic acid,

$$CO_2H\cdot CH_2\cdot CH_2\cdot CHPh\cdot CH(COPh)\cdot CH_2\cdot CO_2H,$$

which forms crystals melting at 132° and is not volatile with steam; on reduction with sodium amalgam, it is reconverted into the original lactonic acid; the *barium* salt is crystalline and the *silver* salt amorphous.

IV. *Polymerisation of Phenylbromobutyrolactone with the Elimination of Hydrogen Bromide.*—[With Franz Stadlmayr.]—A polymerisation similar to that described above is observed when phenylbromobutyrolactone is treated with sodium hydroxide; under the influence of dilute sodium hydroxide, benzoylpropionic acid is alone formed. When 25 per cent. sodium hydroxide is used, a solid substance, the diphenyloctenedilactone, separates, whilst a mixture of three acids can be obtained from the solution. Benzoylpropionic acid can be extracted by carbon disulphide, and the two other acids separated by means of their calcium salts. The two acids are respectively the *diphenylketo-octolactonic acid* and the iso*diphenylketo-octolactonic acid*, and are stereoisomeric, $CO_2Na\cdot CH_2\cdot CHBz\cdot CPh{<}\begin{array}{l}CH_2\cdot CH_2\\ O\text{——}CO\end{array}$. The normal acid crystallises with $3H_2O$ in needles melting at 195—197° when anhydrous; its *calcium* salt, $(C_{20}H_{17}O_5)_2Ca,2\frac{1}{2}H_2O$, crystallising in needles, can only be prepared with difficulty, since the acid very readily passes into the corresponding hydroxy-dibasic acid, the *calcium* salt of which, $C_{20}H_{18}O_6Ca$, is amorphous. When treated in neutral solution with phenylhydrazine hydrochloride and sodium acetate, the acid yields the *anhydride* of the phenylhydrazone, $C_{26}H_{22}O_3N_2$, which forms yellow crystals softening at 50° and decomposing at 70°.

iso*Diphenylketo-octolactonic acid* crystallises in prisms melting at 202—206° and is more stable towards calcium hydroxide than the isomeride, being converted only after heating for several hours into the dibasic hydroxy-acid; the *calcium* salt is anhydrous and crystallises in needles, whilst the *calcium* salt of the dibasic acid is amorphous.

Diphenyloctenedilactone, $\begin{array}{l}CO\text{——}O\\ CH_2\cdot CH_2\end{array}{>}CPh\cdot C{<}\begin{array}{l}CPh\text{—}O\\ CH_2\text{—}CO\end{array}$, obtained as just described, crystallises in needles, decomposing at 210° and melting at 226—227°; by alkali hydroxides it is converted into diphenylketoctolactonic acid, together with a very small quantity of an isomeric acid, $C_{20}H_{18}O_5$, which is separated by means of its calcium salt and melts at 170—171°; it behaves as a monobasic lactonic acid.

K. J. P. O.

Camphorcarboxylic Acid, its Salts, Esters, and Ester Salts. II. Julius W. Brühl and H. Schröder (*Ber.*, 1904, **37**, 3943—3958. Compare this vol., i, 646).—Spectrochemical investigation showed that camphorcarboxylic esters are pure ketonic compounds at the ordinary temperature, whereas their acyl derivatives are pure enolic

compounds and their alkyl derivatives pure ketonic compounds. In such cases, therefore, compounds which are capable of exhibiting tautomerism are obtained as liquids, which do not consist of a mixture of the allelotropic forms.

Solutions of the ester salts in various alcohols are stable and suitable for spectrochemical measurement, although aqueous solutions of such salts are unsuitable owing to the autohydrolysis which they undergo. Sodium was dissolved in a definite amount of a given alcohol and the equivalent amount of ester added, the methyl ester being used with sodium methoxide, the ethyl ester with sodium ethoxide, and so on. This solution was then optically investigated, as were also the corresponding alcohol, sodium alkyloxide, and homogeneous ester.

The data obtained for the molecular refraction of the dissolved ester gave, in every case, numbers higher than those observed for the homogeneous ester. The conclusion is drawn that camphorcarboxylic esters suffer enolisation during salt formation, and that the salts thus formed are enolic compounds.

At high concentrations, the groups in the dissolved ester salts are in the same physical and chemical condition in all solvents. The values obtained for solutions in methyl and ethyl alcohols vary with the concentration, whilst the latter influence has little effect when amyl alcohol is used.

The chemical behaviour of solutions of camphorcarboxylic acid and its derivatives in various solvents is discussed. Camphorcarboxylic acid, its salts, and its ester salts exist in solution sometimes in the unimolecular and sometimes in the polymolecular form according to the particular solvent used. All the unimolecular forms react with alkyl haloids, but none of the polymolecular forms do so. A. McK.

Glyoxylic Acid. HANS MEYER (*Ber.*, 1904, 37, 3591—3592. Compare Tafel and Friedrichs, this vol., i, 849).—*Methyl glyoxylate*, prepared by electrolytic reduction of methyl oxalate, crystallises from methyl formate in colourless leaflets, melts at 53°, and volatilises readily at the ordinary temperature. The *phenylmethylhydrazone* forms silvery leaflets, melts at 158—160°, and dissolves readily in alcohol. The p-*nitrophenylhydrazone* crystallises from acetone or pyridine in small, yellow needles and chars at 170—180°. C. H. D.

Convenient New Method of preparing Normal Pimelic Acid. JULIUS VON BRAUN (*Ber.*, 1904, 37, 3588—3591. Compare Hamonet, this vol., i, 643).—On warming a solution of crude $\alpha\epsilon$-dichloro- or dibromo-pentane (this vol., i, 841, 918) with potassium cyanide, pimelonitrile, $C_5H_{10}(CN)_2$, is obtained as a colourless, odourless liquid, boiling at 171—172° under 12 mm. pressure and yielding pimelic acid on hydrolysis.

Since $\alpha\epsilon$-dichloropentane is prepared from piperidine, and calcium pimelate yields *cyclo*hexanone on distillation, this reaction affords a means of passing from a secondary cyclic base to a cyclic ketone. C. H. D.

Action of Nitric Acid on Ethyl Acetonedicarboxylate. Celso Ulpiani and L. Bernardini (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 331—335).—By the action of fuming nitric acid charged with nitrous vapours on ethyl acetonedicarboxylate, Henry and von Pechmann (Abstr., 1893, i, 397) obtained a compound described by them as the peroxide of ethyl dinitrosoacetonedicarboxylate. The authors find that this compound is accompanied by a nitrogenated oil, which can also be obtained as the sole product of the action of nitric acid, free from nitrous fumes, on ethyl acetonedicarboxylate. This oil is found to be identical with the peroxide of ethyl oximinoacetate obtained by the action of fuming nitric acid on ethyl acetoacetate.

When treated with concentrated ammonia solution, the oil is quantitatively transformed into a compound, $(CHON)_n$, which is identical with the product obtained by Steiner (Abstr., 1876, ii, 288) from concentrated sulphuric acid and ammonium fulminurate and with the compound obtained by the action of concentrated sulphuric acid on nitromalonamide (Ulpiani and Ferretti, Abstr., 1902, i, 430).

T. H. P.

Acetonedipropionic Acid and its Derivatives. Hans von Pechmann and Nevil V. Sidgwick (*Ber.*, 1904, 37, 3816—3829).—*Ethyl ketoheptane-αγεη-tetracarboxylate*,

$$CO[CH(CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et]_2,$$

is readily obtained by the action of sodium ethoxide on ethyl acetonedicarboxylate and ethyl β-iodopropionate. It distils at 220—230° under 12 mm. pressure, but considerable loss results owing to decomposition. When the crude ester is hydrolysed with moderately concentrated hydrochloric acid, *acetonedipropionic acid*,

$$CO(CH_2\cdot CH_2\cdot CH_2\cdot CO_2H)_2,$$

is obtained. This exists in two modifications, which, so far, have not been transformed into each other. The one crystallises from water or from a mixture of chloroform and light petroleum in nodular aggregates melting at 101—102°. It gives no coloration with ferric chloride and is readily soluble in most solvents. *Barium, sodium, copper, silver, zinc*, and *lead* salts have been prepared.

The second modification is insoluble in chloroform, crystallises from hot water in plates melting at 108—109°, and forms only about 20 per cent. of the mixture. Both acids yield the same derivatives. The *dimethyl* ester crystallises from light petroleum in colourless plates melting at 30—31°. The *phenylhydrazone*,

$$NHPh\cdot N\colon C(CH_2\cdot CH_2\cdot CH_2\cdot CO_2H)_2,$$

crystallises from dilute alcohol in colourless needles which turn brown on exposure to the air and completely decompose when kept. It melts and decomposes at 151°, is insoluble in benzene or light petroleum, and does not give Bülow's reaction. The *semicarbazone*, $C_{10}H_{17}O_5N_3$, crystallises from hot water in thick prisms and melts and decomposes at 180—181° when rapidly heated.

On reduction with sodium amalgam, the ketonic acid yields *hydroxyazelaic acid* (*δ-hydroxyheptane-αη-dicarboxylic acid*),

$$OH\cdot CH(CH_2\cdot CH_2\cdot CH_2\cdot CO_2H)_2,$$

which may be purified by aid of its *barium* salt, $C_9H_{14}O_5Ba,4H_2O$. The acid crystallises from chloroform or benzene in small plates melting at 104—105°, and on further reduction with fuming hydriodic acid yields a small amount of azelaic acid.

Acetic anhydride has no action on the ketonic acid (compare Volhard, Abstr., 1892, 432), but when heated alone water is eliminated and a mixture of unaltered acid and 1 : 3-*diketo*cyclo*hexane*-2-*propionic acid*, $CH_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot CO_2H$, is obtained. The new acid crystallises from water in well-developed prisms which sinter at 170° and melt at 180—181°. It possesses all the characteristics of the dihydroresorcinol derivatives (Merling, Abstr., 1894, i, 177; Volhard, *ibid.*, 1897, i, 422). Its *dioxime*, $C_9H_{14}O_4N_2$ forms colourless, rhombic plates, which turn brown at 200° and melt at 203—206°. With semicarbazide, it yields a *compound*, $C_{11}H_{16}O_3N_6$, which melts and decomposes at 278°; in composition, this corresponds with a disemicarbazone minus a molecule of water. Its reaction with phenylhydrazine is complex, and a red, crystalline compound is obtained which gives a deep blue coloration with mineral acids. Nitrous acid reacts with the diketo*cyclo*hexanepropionic acid producing a rupture of the ring, and thus yielding γ-iso*nitroso*-δ-*ketoheptane*-αη-*dicarboxylic acid*, $CO_2H\cdot CH_2\cdot CH_2\cdot C(N\cdot OH)\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, which forms pale yellow crystals melting and decomposing at 133—136°. It does not give the Liebermann reaction, and when warmed with concentrated sulphuric acid and poured on to ice (Beckmann's transformation) it yields glutaric and succinic acids, and hence has the above constitution.

Succinic acid diphenylhydrazide melts at 209—211°. J. J. S.

Anhydroaconitic Acid. RICHARD ANSCHÜTZ and W. BERTRAM (*Ber.*, 1904, 37, 3967—3970. Compare Abstr., 1903, i, 550).—By the action of acetyl chloride on aconitic acid, Easterfield and Sell (Trans., 1892, 61, 1009) obtained an anhydride of aconitic acid. Anhydroaconitic acid, prepared by the action of a chloroform solution of acetyl chloride on aconitic acid, crystallises in octahedra and melts at 76°. When prepared as described by Easterfield and Sell, it also melts at 76° and not at 95° as stated by those authors. The same substance, melting at 76°, may also be obtained by heating aconitic acid at 140° under 15—20 mm. pressure. When an attempt was made to distil anhydroaconitic acid under diminished pressure, carbon dioxide was evolved and itaconic anhydride formed.

When anhydroaconitic acid is quickly heated at 250° under the ordinary pressure, the distillate contains a mixture of itaconic and citraconic anhydrides.

Anhydroaconitic acid probably has the formula

$$CO_2H\cdot CH:C<\begin{matrix}CO-O\\ CH_2\cdot CO\end{matrix}.$$

Anhydromethylocitric acid [*anhydromethoxytricarballylic acid*], prepared by the action of acetyl chloride on methoxytricarballylic acid, separates in prisms and melts at 131°. A. McK.

Ethyl Acetonedioxalate (Desmotropy and the Origin of Colour). RICHARD WILLSTÄTTER and RUDOLF PUMMERER (*Ber.*, 1904, 37, 3733—3740).—The authors prepare ethyl acetonedioxalate by condensing acetone directly with two mols. of ethyl oxalate, instead of isolating, as in Claisen's method, the ethyl sodioacetoneoxalate formed as an intermediate product; in this way, a yield of 78 per cent. that of theory can be obtained. The principal product of the synthesis is the monoenol, $CO_2Et{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CH_2{\cdot}CO{\cdot}CO_2Et$ or

$$CO_2Et{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CO_2Et,$$

which forms nearly colourless crystals, melts at 104°, and has a solubility of 1·6 grams in 100 c.c. of ether. When the monoenol is dissolved in alcohol and sodium hydroxide is added, a crystalline precipitate of the disodium salt of the *dienol*,

$$CO_2Et{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CO_2Et,$$

is obtained; on treating this with less than the calculated quantity of dilute hydrochloric acid, the dienol itself is obtained, melting at 97·5—98·5°. It differs from the monoenol in being yellow and in having pronounced tinctorial properties; it absorbs ammonia vapour to form a *diammonium* salt. The monoenol and the dienol are isodynamic and exist together in different equilibria in different solvents; a drop of water added to the colourless alcoholic solution of the monoenol gives rise to the yellow colour of the dienol. On heating either the aqueous or alcoholic solution of the monoenol, an increase in the colour is produced, showing an increase in the proportion of the dienol present. Traces of alkali increase in a marked manner the amount of the dienol existing in solution, whilst acids destroy the latter and remove its colour.

On boiling ethyl acetonedioxalate for 15 minutes with absolute alcohol, it is converted very largely into ethyl chelidonate, which is best prepared by this method. W. A. D.

Action of Formaldehyde on Inorganic Compounds. LUDWIG VANINO and LORENZ SEEMANN (*Chem. Centr.*, 1904, ii, 1205; from *Pharm. Centr.-H.*, 45, 733—735).—By the action of a solution of formaldehyde (3 mols.) on nitric acid (4 mols.), nitric oxide (4 mols.), carbon dioxide (3 mols.), and water are formed, and by this means nitrous vapours may be rapidly prepared; a small quantity of nitrogen is also formed by secondary actions. When solid ammonium nitrate is heated with paraformaldehyde, nitrogen is liberated in abundance, together with small quantities of nitric oxide; the former results from the action of the aldehyde on nitrous oxide, formic acid being also formed. Nitrous oxide, however, is not attacked by formaldehyde in the cold. Hexamethylenetetramine is not acted on by nitric acid at first, but after a time it becomes yellow, and on prolonged heating it is suddenly decomposed with liberation of nitric oxide. When a 40 per cent. solution of formaldehyde is poured into hot concentrated sulphuric acid, carbon separates at about 90°. When the mixture is kept cold, however, paraformaldehyde is formed, the best yield being obtained with a proportion of 10 of sulphuric acid to 50 of formaldehyde. Paraformaldehyde is also formed by the action

of pyrosulphuric acid. When phosphoric oxide is added to a 40 per cent. solution of formaldehyde, the temperature rises and carbon is formed, but by dissolving phosphoric oxide in a solution of formaldehyde, paraformaldehyde is obtained. E. W. W.

A New Anhydride of Dulcitol. P. CARRÉ (*Compt. rend.*, 1904, 139, 637—639. Compare Abstr., 1903, i, 307; this vol., i, 16, 819). —*Dulcide*, $C_6H_{10}O_4$ or $C_4H_6O_2(CH{\cdot}OH)_2$, an isomeride of mannide obtained by the prolonged action of phosphoric acid on dulcitol in a vacuum at a temperature of 135°, is an optically inactive, yellow liquid, boiling at 198° under 18 mm. pressure, is very hygroscopic, but does not regenerate dulcitol on treatment with water in a sealed tube at 200°, is readily soluble in alcohol or pyridine, and insoluble in ether. *Dulcide diphenylcarbamate*, $C_6H_8O_4(CO{\cdot}NHPh)_2$, obtained by the action of phenylcarbimide on dulcide in pyridine solution, crystallises in white plates melting at 233°. *Dulcide dibenzoate*, $C_6H_8O_4Bz_2$, similarly prepared, crystallises from alcohol in white needles melting at 138°. Dulcide is less readily esterified by phosphoric acid than mannide; the *monophosphoric* ester forms a *barium* salt containing 1 mol. of H_2O, a normal *brucine* salt crystallising with $10H_2O$, and a basic *quinine* salt containing 1 mol. of H_2O. M. A. W.

Hydration of Lactose in Solution. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1904, 26, 1065—1082. Compare Abstr., 1903, ii, 623).— When a solution of lactose hydrate is evaporated at a temperature above 95°, anhydrous lactose, $C_{12}H_{22}O_{11}$, separates in large crystals, whilst at the ordinary temperature the hydrate, $C_{12}H_{22}O_{11},H_2O$, is obtained. When a large excess of the hydrate is shaken with water for a few minutes, a solution is formed the concentration of which, termed the "initial solubility," is independent of the quantity of solid substance used. On continuing the agitation for a longer period at 0°, the concentration of the solution slowly increases from 14·80 millimols. per 100 grams of water, the "initial solubility," at a constantly diminishing rate, to 34·82, the "final solubility," at which it remains constant. At this limiting value, the solution contains that quantity of anhydrous lactose which is in equilibrium with the constant quantity of hydrate, corresponding with the "initial solubility," which the solution always contains. When a substance exhibits a rate of solution, the "maximum rate of solution," independent of contact between the solid and liquid phases, and shows an initial and final solubility, it is possible to derive the velocity and equilibrium of the chemical change taking place in the solution even in cases where the substances involved cannot be separately estimated by any chemical or physical method.

Determinations have been made of the maximum rate of solution of lactose hydrate at 0°, 15°, and 25°, and the results correspond with those required by the law of mass action. The rate of hydration is increased 2·8 times by a rise of temperature of 10°. The rate of solution is greatly accelerated by bases; by the use of $N/1000$ ammonia, the velocity is increased 2·4 times. If $N/10$ ammonia solution is used instead of water, the rate of the hydration reaction is

accelerated to such an extent that the final solubility of the anhydrous sugar can be obtained in a few minutes.

The equilibrium ratio of anhydrous to hydrated lactose was calculated from the initial and final solubilities of the hydrate and was found to be 1·35 at 0°, 1·44 at 15°, and 1·51 at 25°, the degree of hydration decreasing considerably with rise of temperature. The velocity constants of the reactions of hydration and dehydration have been calculated from solubility data and also from the rate of change of optical rotation, concordant values being obtained. The amount of lactose which undergoes hydration and dehydration in one hour in a solution which has reached equilibrium has been calculated from the velocity constant and found to be 1·5 per cent. at 0° and 22·2 per cent. at 25° of the total quantity present.

The method of studying the equilibrium of dissolved substances by the principle of the maximum rate of solution is applicable to any kind of reaction which proceeds slowly in solution. Experiments have been carried out on the rate of solution of barium nitrate, potassium sulphate, sodium chloride, and iodine in water at 0°, of iodine in alcohol and in ether at 0°, and of arsenious oxide in water at 25°. There is no evidence that any slow chemical change takes place during the solution of these substances. It is shown that the slow rate of solution of arsenious oxide is not due to any chemical reaction, but is dependent on the surface of contact between the solid and the solution. It seems probable that under ordinary conditions the oxide comes into contact with the water very slowly on account of a film of air adhering to its surface.
E. G.

Rhodeose and Fucose as Antipodal Isomerides. EMIL VOTOČEK (*Ber.*, 1904, 37, 3859—3862. Compare Abstr., 1900, i, 332; 1901, i, 368; 1903, i, 67; Müther and Tollens, this vol., i, 226).—The phenylosazone of fucose has been prepared and is found to melt at 177—177·5° and not at 158—159° (Tollens). *Rhodeonic acid phenylhydrazide* melts at 206°. There can be no doubt but that fucose and rhodeose are optical antipodes, and this has been confirmed by combining the two to form a *racemic compound*. This melts at 161° and is much less soluble in water than the optical isomerides (ratio of solubilities 1 : 5·4). Its phenylosazone melts at 187°.

Rhodeose is also obtained when convolvulin is hydrolysed with 10 per cent. sulphuric acid under slightly increased pressure.
J. J. S.

Oxidation Products of Parasaccharin. HEINRICH KILIANI and PETER LOEFFLER (*Ber.*, 1904, 37, 3612—3616. Compare this vol., i, 373).—When parasaccharin is heated for seven hours at 45—55° with dilute nitric acid, it is converted into *parasaccharone*, which crystallises from water in leaflets or prisms and melts at 159—160°. Parasaccharone is the lactone of parasaccharonic acid, the constitution of which is expressed either by

$$CO_2H\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot CH_2\cdot OH$$

or by $OH\cdot CH_2\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot CO_2H$.

Calcium parasaccharonate, prepared by the addition of calcium

chloride to the potassium salt, separates in leaflets; the *copper* salt separates in needles.

When parasaccharic acid,

$$OH\cdot CH_2\cdot CH_2\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot CH_2\cdot OH,$$

in the form of its barium salt, is oxidised by concentrated nitric acid, a syrup is obtained which, on neutralisation with sodium hydroxide and subsequent addition of calcium chloride, forms *calcium hydroxycitrate*, which separates from water in plates and crystallises with $18H_2O$. The free *acid*, $C_6H_8O_8,H_2O$, separates in needles or plates and melts at the same temperature as parasaccharone, namely, 159—160°. The *potassium* salt forms glistening pyramids and crystallises with $4H_2O$. The *copper* salt crystallises in pyramids. A. McK.

Ultramicroscopic Observations on Solutions of Pure Glycogen. Madame Z. Gatin-Gruževska and Wilhelm Biltz (*Pflüger's Archiv*, 1904, **105**, 115—120).—Solutions of pure glycogen (this vol., i, 295) have been examined by Raehlmann's method (*Berl. Med. Woch.*, 1904, 186) with a Siedentopf and Zsigmondy ultramicroscope. Raehlmann's results are confirmed, except in the case of extremely dilute solutions, where at most one or two particles could be observed in the field of vision at the same time.

Admixture with dilute saline solutions does not affect the general appearance, but the addition of precipitants, such as acetic acid or alcohol, does so. With acetic acid, a number of particles of the same size and of rapidly changing colour were observed in the field, and the light was found to be polarised. On the addition of absolute alcohol, numerous distinct particles were observed, the number of such increasing with the amount of alcohol, and most of these had a characteristic movement.

These phenomena point to the colloidal nature of glycogen solutions.

J. J. S.

Hydrolytic Products of Sugar Cane Fibre. C. A. Browne, jun. (*J. Amer. Chem. Soc.*, 1904, **26**, 1221—1235).—The reactions of thin sections of the sugar cane with various reagents are given. By the action of zinc chloride and iodine, no coloration is produced, showing that the cellulose is completely combined with other substances. After boiling with dilute sodium hydroxide, however, the blue coloration characteristic of cellulose is obtained without difficulty. A proximate analysis of the different tissues of the sugar cane has been made, and the results show that the degree of lignification is greatest in the rind and smallest in the pith.

The fibre of the sugar cane was digested with 5 per cent. solution of sodium hydroxide at 100° for 8 hours. On treating the liquid with 95 per cent. alcohol, a precipitate of cane gum was obtained, which, when dry, amounted to 25 per cent. of the original fibre. This substance dissolved sparingly in hot water, forming an opalescent solution, had $[\alpha]_D - 83\cdot2°$, and on distilling with hydrochloric acid yielded 44·88 per cent. of furfuraldehyde equivalent to 76·43 per cent. of pentosans; it contained 12 per cent. of inorganic matter.

When the gum was heated at 100° for 10 hours with 4 per cent. hydrochloric acid, xylose and arabinose were produced in proportions which indicate that xylan and araban constitute nearly 80 per cent. of the gum in the probable ratio of about five of the former to one of the latter.

The alkaline filtrate from the gum was evaporated until all the alcohol had been expelled, and was afterwards acidified with dilute sulphuric acid. A dark brown precipitate of lignin was obtained, which, when dry, amounted to 10·78 per cent. of the weight of the original fibre. The dry product formed a brown powder, soluble in water or alcohol; when heated with hydrochloric acid, it gave no trace of furfuraldehyde. The acid filtrate from the lignin precipitate contained a quantity of acetic acid corresponding with 5·23 per cent. of the original fibre.

The fibre, after being treated with sodium hydroxide, was washed with hot water and alcohol; it was then of a light straw colour, and amounted to about 42 per cent. of the original material. On distilling with hydrochloric acid, it yielded 5·07 per cent. of furfuraldehyde. When this fibre was hydrolysed with sulphuric acid, dextrose was produced. E. G.

Alkylamines containing Fluorine. FRÉDÉRIC SWARTS (*Bull. Acad. Roy. Belg.*, 1904, 955—969. Compare this vol., i, 853).—When difluorobromoethane is heated with ammonia dissolved in alcohol at 160—170°, ethyl ether, difluoroethylamine, tetrafluorodiethylamine, and *tetrafluorotriethylamine*, $NEt(CH_2 \cdot CHF_2)_2$, are formed.

The last of these may be separated from the associated secondary amine by converting this into the nitroso-derivative, distilling the mixture, and dissolving out the tertiary amine with hydrochloric acid and regenerating and purifying in the usual way. Tetrafluorotriethylamine is a colourless liquid with an odour recalling that of chloroacetal; it boils at 137° under 754 mm. pressure, and is almost insoluble in water. It is a very weak base, and aqueous solutions of its salts are acid to indicators; the *hydrochloride*, obtained by the action of hydrogen chloride on the amine dissolved in ether, is deliquescent. The amine decomposes at a red heat forming hydrogen fluoride and hydrogen cyanide. The electrical conductivity of the base could not be determined, but for the hydrochloride, $\mu_{1024} - \mu_{32}$ was approximately equal to 170. Tetrafluorotriethylamine is not produced by the action of ethyl alcohol on tetrafluorodiethylamine itself, but only in presence of haloid salts of this or of the primary amine, which seem to behave like zinc and stannic chlorides (compare Merz and Gasiorowski, Abstr., 1884, 984). The etherification of the alcohol in the foregoing reaction is due to the action of the haloid salts of the amines, and experiments showed that the salts of tetrafluorodiethylamine were more active than those of difluorethylamine in this respect, which appears to indicate that the etherification is really brought about by the acids liberated by the hydrolysis of the haloid salts of the amines. Reynoso observed (*J. pr. Chem.*, 1857, [i], 69, 52) that small quantities of ether were produced by heating hydrochlorides of morphine and cinchonine with alcohol at 200°. T. A. H.

Action of Ammonia and Ethylamine on the Esters of Sulphonic Acids. WILHELM AUTENRIETH and RENÉ BERNHEIM (*Ber.*, 1904, 37, 3800—3809. Compare Carius, *J. pr. Chem.*, 1870, [ii], 2, 262).—Cold alcoholic ammonia reacts with the esters of both aliphatic and aromatic sulphonic acids yielding an alkylamine salt, $R\cdot SO_2\cdot OR' + NH_3 = R\cdot SO_2\cdot ONH_3R'$; a considerable amount, however, of the ammonium salt of the acid is formed at the same time. Sulphonamides are either not formed or formed only in minute quantities. The formation of the ammonium and alkylamine salts is probably due to the liberation of the free acid by the action of ammonia on the ester, $R\cdot SO_2\cdot OEt + NH_3 = R\cdot SO_2\cdot OH + NH_2Et$, and the free acid then combines with the excess of ammonia and the liberated amine according to the laws of mass action. With butyl benzenesulphonate, no butylamine salt is formed.

The ethyl esters of ethanesulphonic acid, benzenesulphonic acid, ethane-$\alpha\beta$-disulphonic acid, ethane-$\alpha\alpha$-disulphonic acid, and of propane-$\alpha\gamma$-disulphonic acid have been treated in this way, also methyl benzenesulphonate. Concentrated aqueous ammonia may be used in place of the alcoholic with similar results.

Ethyl benzenesulphonate and ethylamine yield a small amount of *diethylamine benzenesulphonate* melting at 139°. Ethyl ethanesulphonate and ethyl benzenesulphonate with aniline gave small amounts of the corresponding *aniline* salts melting respectively at 142° and 234°. The formation of these was probably due to the presence of a small amount of free acid in the esters.

Ethyl ethane-$\alpha\beta$-disulphonate crystallises in long prisms and melts at 77·5°.

Most of the salts were obtained by the addition of ether and are hygroscopic. The presence of ethylamine was detected by conversion into benzenesulphonethylamide (m. p. 58°). J. J. S.

Abnormal Salt-formation in the Case of the Trialkyltrimethylenetriamines. ALFRED EINHORN and AUGUST PRETTNER (*Annalen*, 1904, 334, 210—233. Compare Abstr., 1902, i, 840).—It has been shown (*loc. cit.*) that the hydriodide of triethyltrimethylenetriamine, $CH_2<\begin{matrix}NEt\cdot CH_2\\ NEt\cdot CH_2\end{matrix}>NEt$, is converted to the extent of 10 per cent., when heated, into an isomeric hydriodide, which behaves as a quaternary ammonium salt. Both compounds can also be obtained from the methiodide of triethyltrimethylenetriamine, the normal salt being produced when the alcoholic solution is allowed to evaporate at a low temperature, and the quaternary salt when the alcoholic solution is boiled before evaporation. Towards alkali carbonates and hydroxides, these salts behave differently; from the normal salt, the base is completely displaced, whilst the quaternary salt is unchanged by potassium carbonate and by potassium hydroxide at a low temperature, but at a higher temperature is decomposed, yielding a mixture of triethyltrimethylenetriamine and an ammonium base. The same base, which could not be isolated, is also obtained by using silver oxide; its solution can be reconverted into the iodide. Two series of picrates and bromides exist. From the fact that the abnormal iodide

can be directly converted into the picrate, a behaviour characteristic of quaternary salts, whilst the normal salt is merely decomposed by picric acid, it is concluded that the abnormal salt is a quaternary compound. All the quaternary salts are able to form additive compounds with iodoform, whilst the normal salts are not.

After discussion, it is suggested that this isomerism is best accounted for on Werner's hypothesis (Abstr., 1902, ii, 554), according to which the normal salt would be a "hydronium" compound,

$$CH_2{<}\begin{matrix}NEt{\cdot}CH_2\\NEt{\cdot}CH_2\end{matrix}{>}NEt,HI,$$

and the abnormal salt a "carbonium" salt,

$$CH_2{<}\begin{matrix}NEt{\cdot}CH_2\\NEt{\cdot}CH_2\end{matrix}{>}NH,EtI.$$

Triethyltrimethylenetriamine (b. p. 196—198°) is prepared by adding an ice-cold solution of ethylamine to a 40 per cent. solution of formaldehyde. The normal *hydriodide* (m. p. 121°) has a faint alkaline reaction, is decomposed by prolonged boiling of its aqueous solution, and immediately on addition of picric acid or dilute hydrochloric acid, an oil being formed; platinic chloride also decomposes the salt, with the production of ethylamine platinichloride. The hydrobromide crystallises in needles melting and decomposing at 123°. The *picrate*, $(CH_2{\cdot}NEt)_3,C_6H_2(NO_2)_3{\cdot}OH$, prepared by bringing together the components in ethereal solution, crystallises in pale yellow needles and sinters and melts at 65°; the *dipicrate* is prepared in a similar manner. The *methiodide*, $(CH_2{\cdot}NEt)_3,MeI$, formed by adding methyl iodide to an ethereal solution of the base, is a hygroscopic, white powder melting at 98—99°.

The abnormal *hydriodide*, prepared as previously described, crystallises in three-cornered leaflets melting at 199—200°, is neutral in aqueous solution, and is stable on heating. The *additive* compound with iodoform, $C_3H_6Et_3N_3,HI,CHI_3$, formed on bringing the components together in methyl alcoholic solution, crystallises in needles melting at 133—134°. The *hydrobromide* is prepared by shaking a solution of the iodide with silver bromide and crystallises in hexagonal plates melting at 182°; the *platinichloride* crystallises in rhombic needles decomposing at 215°; the *picrate*, readily prepared directly from the hydriodide, crystallises in yellow needles melting at 108°.

Trimethyltrimethylenetriamine yields also two series of salts. The *methiodide* of the base is prepared by bringing the components together in ethereal solution, and is very hygroscopic. The normal *hydriodide* melts and decomposes at 116°, and when heated at 116—135° is converted into a salt melting at 150—152°, which is not homogeneous, but a mixture of an isomeric hydriodide with trimethylamine hydriodide; a similar mixture is obtained when the alcoholic solution of the methiodide is boiled. The salts can be separated by converting the quaternary ammonium compound into the additive compound with iodoform, which is more soluble than the corresponding *additive* compound with trimethylamine, NMe_3,HI,CHI_3; the latter crystallises in pale yellow needles melting at 200°; the *additive* compound of the ammonium base, $C_6H_3Me_3N_3,HI,CHI_3$, crystallises in needles melting at 125°. The abnormal *hydriodide* prepared from the iodoform

additive compound crystallises in six-sided plates melting at 166°, and can be obtained unchanged from its aqueous solution. The corresponding *picrate*, prepared from the hydriodide, melts at 159—160°.

The *methiodide* of hexamethylenetetramine, $C_6H_{12}N_4$,MeI, prepared by prolonged heating of methyl iodide and hexamethylenetetramine iodide in alcoholic solution, crystallises in needles melting at 204°, and reacts with picric acid, yielding the *picrate*,

$$C_6H_{12}N_4Me\cdot O\cdot C_6H_2(NO_2)_3,$$

which crystallises in yellow needles melting at 215°. K. J. P. O.

Triaminoguanidine. ROBERT STOLLÉ (*Ber.*, 1904, 37, 3548—3549).—*Triaminoguanidine hydrochloride*, $NH_2\cdot N\colon C(NH\cdot NH_2)_2$,HCl, formed when hydrazine hydrate is boiled with an excess of carbon tetrachloride in a current of ammonia in a reflux apparatus for some days, crystallises from alcohol in slender needles and melts and decomposes at 228°. The *tribenzylidene* derivative, obtained, along with benzylideneazine, by shaking the aqueous solution of the crude hydrochloride with benzaldehyde, crystallises in yellow, microscopic needles, melts at 196°, and, when boiled with dilute hydrochloric acid, yields benzaldehyde, *s*-diaminocarbamide, and a condensation *product* which melts at about 240°. G. Y.

Esters of Nitrogentricarboxylic Acid and Similar Compounds. OTTO DIELS and PAUL NAWIASKY (*Ber.*, 1904, 37, 3672—3683. Compare Abstr., 1903, i, 324).—*Methyl ethyl iminodicarboxylate*, $CO_2Me\cdot NH\cdot CO_2Et$, obtained by the action of methyl chlorocarbonate on the sodium derivative of urethane, crystallises from a mixture of ether and light petroleum in glistening needles melting at 73° after sintering at 68°. It dissolves readily in most solvents, and with concentrated potassium hydroxide yields a precipitate of the *potassium* derivative. The same ester is formed by the action of ethyl chlorocarbonate on the sodium derivative of methyl carbamate.

Dimethyl ethyl nitrogentricarboxylate, $CO_2Et\cdot N(CO_2Me)_2$, obtained by the action of methyl chlorocarbonate on the disodio-derivative of urethane, is a colourless liquid, distilling at 131° under 8 mm. or at 144—145° under 12·5 mm. pressure. It has n_D 1·43386 and the sp. gr. 1·2146 at 22°. When hydrolysed with cold potassium hydroxide, the ester yields methyl ethyl iminodicarboxylate, carbon dioxide, and methyl alcohol. With cold 25 per cent. ammonia, it yields methyl and ethyl allophanates, cyanuric acid, and methyl and ethyl carbamates.

Ethyl diamyl nitrogentricarboxylate, obtained by the action of amyl chlorocarbonate on disodiourethane, is a clear oil distilling at 184—186° under 13 mm. pressure, has a sp. gr. 1·0380 at 15°, and is strongly refractive.

Dicarbethoxyglycine ester (*ethyl dicarbethoxyaminoacetate*),

$$N(CO_2Et)_2\cdot CH_2\cdot CO_2Et,$$

obtained by the action of ethyl chlorocarbonate on carbethoxyglycine ester, crystallises from light petroleum in stout prisms melting at 36·5° and boiling at 152—153° under 10 mm. pressure. With ammonia, at 20—30°, it yields carbethoxyglycinamide.

Ethyl dicarbethoxy-oxamate, $N(CO_2Et)_2\cdot CO\cdot CO_2Et$, obtained by the action of ethyl oxalyl chloride, $COCl\cdot CO_2Et$ (boiling at 133—135°), on the potassium derivative of ethyl iminodicarboxylate, is a colourless oil, which distils at 170·5—171·5° under 11 mm. pressure, does not solidify in a freezing mixture, and has a sp. gr. 1·1752 at 17°.

Ethyl iminodioxalate, $NH(CO\cdot CO_2Et)_2$, obtained from ethyl sodiocarbamate and ethyl oxalylchloride, melts at 71—72°.

Ethyl diethoxalylcarbamate, $CO_2Et\cdot N(CO\cdot CO_2Et)_2$, is obtained, together with the ethyl carbethoxycarbamate (m. p. 47°), from disodiourethane and ethyl oxalylchloride. It is a colourless oil, distilling at 182—184° under 9—10 mm. pressure, has a sp. gr. 1·2294 at 16°, and on hydrolysis in the cold yields potassium oxalate.

*Ethyl aniline-*N*-dicarboxylate*, $NPh(CO_2Et)_2$, obtained by the action of ethyl carbonate on sodiophenylurethane, crystallises from acetone and light petroleum in large prisms, which sinter at 58° and melt at 62°. It dissolves readily in most solvents, is stable towards alkalis, and with ammonia yields phenyl urethane.

*Methyl ethyl aniline-*N*-dicarboxylate*, $CO_2Me\cdot NPh\cdot CO_2Et$, obtained by using methyl chlorocarbonate, sinters at 65°, melts at 69°, is only sparingly soluble in ether, and is very sparingly soluble in water, light petroleum, or concentrated hydrochloric acid. *Methyl aniline-*N*-dicarboxylate*, $NPh(CO_2Me)_2$, melts at 142—143° and crystallises from ether in quadratic plates. *Ethoxalylaniline-*N*-carboxylate*,

$$CO_2Et\cdot NPh\cdot CO\cdot CO_2Et,$$

sinters at 64°, melts at 68°, and distils at 188—190° under 8—9 mm. pressure.

J. J. S.

Alkylated Aminoacetonitriles. EMIL KNOEVENAGEL and ERNST MERCKLIN (*Ber.*, 1904, **37**, 4087—4094. Compare this vol., i, 989).—*Sodium diethylaminomethanesulphonate*, $NEt_2\cdot CH_2\cdot SO_3Na$, formed by the action of diethylamine on formaldehyde and sodium hydrogen sulphite in aqueous solution, separates from alcohol in crystals, when heated on platinum, swells up, burns, melts, and leaves a carbonaceous residue, and yields tetraethylmethylenediamine when heated with dilute hydrochloric acid, with aqueous potassium hydroxide, or with phosphorus pentachloride and alcohol successively. *Acetyldiethylaminomethanol*, $NEt_2\cdot CH_2\cdot OAc$, formed when sodium diethylaminomethanesulphonate is boiled with acetic anhydride, boils at 81—82° under 14·5 mm. pressure. Diethylaminoacetonitrile, formed by the action of potassium cyanide on the sodium sulphonate, boils at 62·5° under 14 mm. pressure; the methiodide melts at 186°, the hydrochloride crystallises in small, white needles and melts at 186° (Klages and Margolinsky, this vol., i, 146).

α-Diethylaminopropionitrile is formed by the action of aqueous potassium cyanide on the additive compound of diethylamine, acetaldehyde, and sodium hydrogen sulphite (Klages and Margolinsky, *loc. cit.*). *α-Diethylamino*iso*hexonitrile*, obtained similarly from *iso*valeraldehyde, boils at 88·5—89° under 11 mm. pressure; *α-diethylamino-*n*-octonitrile*, $NEt_2\cdot CH(C_6H_{13})\cdot CN$, obtained from heptaldehyde, boils at 125—126° under 11 mm. pressure; α-diethylaminobenzyl cyanide, formed from

benzaldehyde, boils at 130—131° under 11 mm. pressure (Klages and Margolinsky, *loc. cit.*); *a-diethylamino-*p*-methoxybenzyl cyanide*, obtained from anisaldehyde, crystallises in white needles, melts at 44°, boils at 166° under 11 mm. pressure, and is hydrolysed by concentrated sulphuric acid and aqueous alcoholic sodium hydroxide to *a-diethylamino-*p*-methoxyphenylacetamide*, which crystallises in small, white needles and melts at 161°. The *methylene ether* of diethylamino-3 : 4-dihydroxyphenylacetonitrile, obtained from piperonal, melts at 43—44° and boils at 179·5° under 12·5 mm. pressure.

Ethylaminoacetonitrile, $NHEt\cdot CH_2\cdot CN$, boils at 81—83° under 29 mm., or at 166—167° under atmospheric pressure; with phenylcarbimide, it forms the *phenylcarbamide*, $NHPh\cdot CO\cdot NEt\cdot CH_2\cdot CN$, which sinters at 107° and melts at 116°. The *phenylthiocarbamide*, $C_{11}H_{13}N_3S$, crystallises in yellow needles and melts at 184—185°.

Ethyliminobisacetonitrile, $NEt(CH_2\cdot CN)_2$, is a colourless oil and boils at 141° under 13 mm. pressure; the *hydrochloride*, $C_6H_{10}N_3Cl$, crystallises in white needles and melts at 110—112°.

*a-Ethylamino*iso*hexonitrile*, $NHEt\cdot CH(C_4H_9)\cdot CN$, obtained from *iso*valeraldehyde, boils at 83·5—84° under 12 mm. pressure; *a-ethylamino-*n*-octonitrile*, $NHEt\cdot CH(C_6H_{13})\cdot CN$, boils at 122° under 12 mm. pressure. G. Y.

Derivatives of Glycollonitrile. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1904, 895—906. Compare Abstr., 1890, i, 739; 1899, i, 182, 183, 255, and 567).—When chloroacetonitrile is warmed with dry potassium formate, *cyanomethyl formate*, $H\cdot CO_2\cdot CH_2\cdot CN$, is produced. This is a colourless liquid with a slight odour; it boils at 172—173° under 759 mm. pressure, has a sp. gr. 1·182 at 20° and n_D 1·40918 at 20°, and is hydrolysed by water into glycollonitrile and formic acid; with methyl alcohol, the latter is eliminated as methyl formate. *Cyanomethyl acetate*, $CN\cdot CH_2\cdot OAc$, similarly prepared, boils at 179—180° under 75 mm. pressure, has a sp. gr. 1·105 at 20° and n_D 1·4107 at 20°. It is only slowly hydrolysed by boiling water, forming glycollonitrile as one product.

Cyanomethyl propionate is a colourless liquid possessing a slight odour. It boils at 188—189° under 759 mm. pressure, has a sp. gr. 1·062 at 20° and n_D 1·41662 at 20°. *Cyanomethyl* n*-butyrate* is a liquid with a faint butyric odour; it boils at 200° under 758 mm. pressure and has n_D 1·42131 at 20°. Comparison of the boiling points of these cyano-derivatives with those of the ethyl esters of the same acids show that the value of the increase in boiling point due to the replacement of a CH_3-group by the CN-group decreases as the series is ascended. Chloroacetonitrile reacts readily with ammonia and with primary and secondary amines, but the cyanoamines of the type $CN\cdot CH_2\cdot NX_2$ so formed are more readily obtained by the interaction of glycollonitrile with the secondary amines. Comparing these cyanoamines with the corresponding ethylamines, it is seen that here also the replacement of $-CH_3$ by $CN-$ results in an elevation of the boiling point, and the value of this increment decreases as the series is ascended.

T. A. H.

Double Cyanides of Mercury. HERMANN GROSSMANN and PETER VON DER FORST (*Ber.*, 1904, 37, 4141—4144).—The *potassium* salt has the composition $K_2Hg(CN)_4$, and the *sodium* salt $NaHg(CN)_3$, but conductivity measurements show the presence of double molecules, $Na_2Hg_2(CN)_6$. The *barium* and *strontium* compounds crystallise in needles, their composition being $BaHg(CN)_4,3H_2O$ and $SrHg(CN)_4,5H_2O$ respectively. The *calcium* salt, $CaHg_2(CN)_6,3H_2O$, crystallises in colourless, very hygroscopic needles, whilst $Ca_2Hg_3(CN)_{10},6H_2O$ forms four-sided platelets. The *magnesium* salt has the composition $Mg_2Hg_3(CN)_{10},5H_2O$. E. F. A.

New Method of preparing Organic Derivatives of Phosphorus. VICTOR AUGER (*Compt. rend.*, 1904, 139, 639—641).—By the action of methyl iodide on a solution of phosphorus in alcoholic sodium hydroxide containing water (compare Michaelis and Pitsch, Abstr., 1900, ii, 137; 1903, ii, 207), a mixture of primary, secondary, and tertiary phosphines are obtained and isolated after oxidation as methylphosphinic acid, dimethylphosphinic acid, and trimethylphosphine oxide respectively; when *iso*amyl iodide replaces methyl iodide in the above reaction, the principal products are *iso*amylphosphinic acid and di*iso*amylphosphinic acid.

Attempts to prepare normal sodium phosphite, Na_3PO_3, by the action of excess of sodium ethoxide on an alcoholic solution of phosphorous acid were unsuccessful, disodium hydrogen phosphite, Na_2HPO_3, being the only product; the author therefore concludes that Zimmermann's normal sodium phosphite does not exist (compare Abstr., 1874, 655). M. A. W.

Action of the Halogen Derivatives of Tervalent and Quinquevalent Metalloids on Alkyl Haloids. VICTOR AUGER (*Compt. rend.*, 1904, 139, 671—672. Compare preceding abstract).—A mixture of the periodides of the mono-, di-, and tri-alkyl-phosphines, of which two-thirds is the di-substituted compound, is obtained by the action of phosphorus di-iodide and methyl, ethyl, or propyl iodide in the proportion of 3RI to P_2I_4 at 180—210°, and a similar reaction is obtained when phosphorus tribromide or trichloride replaces the phosphorus di-iodide. Arsenic chloride does not react with ethyl or methyl iodide even at 210°; antimony chloride and ethyl iodide at 150—160° give antimony iodide and ethyl chloride, together with a small quantity of an ethyl derivative of antimony which has not yet been separated; bismuth chloride and ethyl iodide give only bismuth iodide and ethyl chloride. M. A. W.

Action of Organomagnesium Solutions on the Halogen Derivatives of Phosphorus, Arsenic, or Antimony. VICTOR AUGER and M. BILLY (*Compt. rend.*, 1904, 139, 597—599. Compare this vol., i, 22, 724).—Magnesium methyl iodide reacts with phosphorus di-iodide at the ordinary temperature to form tetramethylphosphonium iodide, and with phosphorus trichloride at −20° to form tetramethylphosphonium chloride and phosphorus di-iodide; if, how-

ever, the crude product is treated with nitric acid and sodium nitrite, red crystals of *tetramethylphosphonium periodide*, $PMe_4I:I_2$, are obtained. Magnesium methyl bromide at $-30°$ gives, with phosphorus trichloride, a mixture of mono-, di-, and tri-alkyl substituted derivatives of phosphine, which, on oxidation, yield monomethylphosphinic acid, dimethylphosphinic acid, and trimethylphosphine oxide respectively, the yield of the disubstituted derivative being equal to the sum of the other two.

Magnesium ethyl bromide reacts at low temperatures with arsenic trichloride, and the product, after oxidation, consists principally of triethylarsine oxide, together with small quantities of monomethylarsonic acid and diethylarsonic acid.

Ethylstibine iodide, $SbEtI_2$, crystallising in golden-yellow scales melting at 43° and decomposing at 200°, is isolated by the action of potassium iodide on the mixed product obtained from the action of magnesium ethyl bromide on antimony trichloride at $-18°$.

M. A. W.

Amphoteric Nature of Cacodylic Acid. JOHN JOHNSTON (*Ber.*, 1904, 37, 3625—3627. Compare Zawidzki, Abstr., 1903, i, 801; this vol., i, 232, 564; Hantzsch, this vol., i, 725).—In the determinations of the electrical conductivity of aqueous solutions of cacodylic acid made by Zawidzki, the water used by him was not sufficiently pure to permit of his results at large dilutions being of theoretical importance. The author has measured the conductivity of aqueous solutions of cacodylic acid at 25°, using water with $K = 0·65 \times 10^{-6}$ at 18°. From the figures quoted, the Ostwald "constant" increases very considerably, and this points to the amphoteric nature of the acid. The acid constant, k_a, is taken as $6·4 \times 10^{-7}$, the ratio k_b/K as 32, μ_∞ (acid) as 354·5, and μ_∞ (salt) as 61. The experimental values are in accordance with the theory advanced by Walker (this vol., ii, 509).

A. McK.

Nitration of *o*-Dichlorobenzene. RUDOLF NIETZKI and ADOLF KONWALDT (*Ber.*, 1904, 37, 3892—3893).—*o*-Dichlorobenzene yields two dinitro-derivatives on nitration, which may be separated by fractional crystallisation.

1 : 2-*Dichloro*-4 : 5-*dinitrobenzene* melts at 114° and yields the dichloronitroaniline melting at 175° when heated with alcoholic ammonia. One nitro-group is removed by heating with aniline hydrochloride.

1 : 2-*Dichloro*-3 : 4-*dinitrobenzene* melts at 53—55° and loses both atoms of chlorine when heated with ammonia, the nitro-groups remaining intact (compare Hartley and Cohen, Trans., 1904, 85, 867).

C. H. D.

Magnesium Amalgam as a Reducing Agent. THOMAS EVANS and WILLIAM C. FETSCH (*J. Amer. Chem. Soc.*, 1904, 26, 1158—1161).—Magnesium amalgam containing 5 or 10 per cent. of magnesium may be readily prepared by triturating mercury with powdered magnesium, the latter being added in small quantities at a time. The amalgam decomposes water rapidly with evolution of hydrogen, but is without action on cold, dry alcohol, and is therefore a convenient

reagent for the preparation and preservation of absolute alcohol. When alcohol is boiled for a long time with the amalgam, hydrogen is liberated and a pale yellow solution is obtained which, on evaporation and ignition, yields a very small residue of magnesium oxide.

When a strong alcoholic solution of nitrobenzene is treated with magnesium amalgam in slight excess of the quantity theoretically required to reduce it to phenylhydroxylamine, hydrogen is evolved and azobenzene is obtained in a yield amounting to 95·66 of the theoretical. No hydrazobenzene is produced in this reaction.

E. G.

Reducing Action of Magnesium Amalgam on Aromatic Nitro-compounds. THOMAS EVANS and HARRY S. FRY (*J. Amer. Chem. Soc.*, 1904, 26, 1161—1171).—When a dilute solution of nitrobenzene in 93 per cent. ethyl alcohol is treated with the quantity of magnesium amalgam theoretically required to convert it into aniline and, after the whole of the amalgam has been decomposed, the solution is heated for 15 hours under a reflux condenser, azoxybenzene is produced, the yield amounting to 89·9 per cent. of the theoretical. If methyl alcohol is used instead of ethyl alcohol, an 88·5 per cent. yield of azobenzene is obtained.

When *m*-dinitrobenzene is similarly treated with magnesium amalgam in presence of ethyl alcohol, *m*-dinitroazoxybenzene is produced, the yield amounting to 70 per cent. of the theoretical. If methyl alcohol is employed, the same product is obtained, but the yield is only 54·37 per cent.

o-Nitrotoluene is reduced by magnesium amalgam in presence of ethyl alcohol with formation of a 50 per cent. yield of *o*-azoxytoluene, whilst in presence of methyl alcohol a 66·5 per cent. yield of *o*-azotoluene is obtained.

p-Nitrotoluene in solution in ethyl alcohol gives a 90 per cent. yield of *p*-azoxytoluene, whilst with methyl alcohol the product consists of 22·2 per cent. of the theoretical yield of *p*-azoxytoluene, 23·9 per cent. of that of *p*-azotoluene, and 38 per cent. of unchanged *p*-nitrotoluene.

These results show that when a dilute solution of a nitro-compound in ethyl alcohol is reduced with magnesium amalgam, an azoxy-derivative is formed, whilst in methyl alcohol solutions there is a tendency for the azo-derivative to be produced. The following experiments were undertaken with a view to ascertain the cause of this difference in the behaviour of the two alcohols.

When pure dry methyl alcohol is heated with magnesium amalgam, magnesium methoxide is produced, which gradually separates from the cold solution in long, prismatic crystals. If ethyl alcohol is heated with the amalgam, magnesium ethoxide is formed as an insoluble precipitate. It is probable, therefore, that the reason that the reduction proceeds further in dilute methyl alcohol than in dilute ethyl alcohol solution is that the magnesium methoxide is soluble, and is therefore readily oxidised to the formate, whilst the ethoxide, being insoluble, has a much weaker reducing action. In order to obtain confirmation of the reducing action of the methoxide, a solution of

nitrobenzene in methyl alcohol was treated with magnesium amalgam without the application of heat. In this case, azoxybenzene was formed as the chief product of the reduction, together with a smaller quantity of azobenzene. It is evident, therefore, that the azoxybenzene is formed first, and is subsequently reduced to azobenzene when boiled with a solution of magnesium methoxide.

It has been shown by Evans and Fetsch (preceding abstract) that when a strong solution of nitrobenzene in ethyl alcohol is reduced by magnesium amalgam, azobenzene is the chief product of the reaction. When a concentrated solution of *p*-nitrotoluene in 95 per cent. ethyl alcohol is similarly treated, a mixture of *p*-azotoluene and *p*-azoxytoluene is produced. It is probable that the greater reducing action of the amalgam in the hot concentrated solution is due to part of the magnesium ethoxide undergoing oxidation as it is formed. When, however, the reduction is carried out in a cold solution, the ethoxide is precipitated and consequently takes no further part in the reaction. E. G.

Influence of the Cathode Material on the Reduction of *m*- and *p*-Nitrotoluenes. WALTHER LÖB and JOS. SCHMITT (*Zeit. Elektrochem.*, 1904, 10, 756—764).—The nitro-compounds are suspended in 2 per cent. sodium hydroxide solution contained in a porous pot; cathodes of nickel, zinc, and of copper with and without copper dust are used. The products in every case were the azoxytoluene, hydrazotoluene, and toluidine. When *p*-nitrotoluene is used, some *p*-azotoluene is also formed. The most feeble reduction is observed with nickel; zinc, copper, and copper + copper dust giving more energetic reduction in the order mentioned. Not only is the current efficiency better with the last-named cathode, but the reduction goes further, toluidine being the predominant product with copper, whilst azoxytoluene is the main product with nickel. *p*-Nitrotoluene is more easily reduced than *m*-nitrotoluene. The electrolytic reduction of *m*-nitrotoluene with a nickel cathode might be employed as a method of preparation of *m*-azoxytoluene, and the toluidines might be suitably prepared by reduction with a copper cathode in presence of copper dust, but the other reductions studied lead to mixtures of substances which are only separated from each other with great difficulty. T. E.

Tetrahydro- and Decahydro-naphthalenes. HENRI LEROUX (*Compt. rend.*, 1904, 139, 672—674).—Tetrahydronaphthalene, $C_{10}H_{12}$, obtained by the direct hydrogenation of naphthalene at 180° by Sabatier and Senderens' method (compare Abstr., 1901, i, 459), is a colourless liquid boiling at 206° (corr.), has a sp. gr. 0·984 at 0° or 0·966 at 20°, and n_D 1·5402 at 20°, and yields, on oxidation with potassium permanganate, *o*-carboxyhydrocinnamic acid. *Chlorotetrahydronaphthalene,* $C_{10}H_{11}Cl$, obtained by the direct action of chlorine on tetrahydronaphthalene, boils at 121—124° under 15 mm., or at 230° under atmospheric pressure, evolving hydrogen chloride. *Bromotetrahydronaphthalene,* $C_{10}H_{11}Br$, obtained by the action of bromine on the hydrocarbon, boils at 145—147° under 21 mm. and distils and decomposes at 250° under atmospheric pressure. Tetrahydronaphtha-

lene bromohydrin, $C_{10}H_{10}Br{\cdot}OH$, formed, together with the preceding compound, by the action of bromine on tetrahydronaphthalene, crystallises from acetone in magnificent prisms melting at 112° (corr.), and may be identical with the bromohydrin obtained by Bamberger and Lodter (compare Abstr., 1893, i, 591) by the action of hydrogen bromide on tetrahydronaphthylene oxide. *Decahydronaphthalene*, $C_{10}H_{18}$, obtained by hydrogenating tetrahydronaphthalene at 175°, is a colourless liquid with an odour of menthol, boils at 187—188° (corr.), has a sp. gr. 0·893 at 0° or 0·877 at 20°, and n_D 1·4675 at 20°, and differs in its physical properties from the compound of the same composition described by Wreden and Znatowick (compare Abstr., 1877, 899); it reacts readily with chlorine forming *chlorodecahydronaphthalene*, $C_{10}H_{17}Cl$, boiling at 112—115° under 18 mm. pressure, and *dichlorodecahydronaphthalene*, $C_{10}H_{16}Cl_2$, boiling at 145—148° under 18 mm. pressure. M. A. W.

Terpenes and Ethereal Oils. LXVIII. Nitrites of some Cyclic Hydrocarbons. OTTO WALLACH [with ERICH BESCHKE] (*Annalen*, 1904, **336**, 1—8. Compare this vol., i, 753).—Indene nitrite, obtained in the same manner as anethole nitrite (*loc. cit.*), yields β-nitroindene, which melts at 141°, when distilled in small quantities in a current of steam (Dennstedt and Ahrens, Abstr., 1895, i, 475). β-Hydrindone is obtained when β-nitroindene is reduced with zinc dust and acetic acid and the product hydrolysed with dilute sulphuric acid; the *semicarbazone*, $C_{10}H_{11}ON_3$, melts at 203—205°.

3-*Methylindene nitrosochloride* is a white, crystalline powder. 2-*Nitro-3-methylindene*, $C_{10}H_9O_2N$, obtained along with an acid substance by the action of steam on 3-methylindene nitrosochloride, or by treatment of 3-methylindene with sodium nitrite in alcoholic acetic acid solution, forms large, yellow crystals, melts at 107—108°, and, when reduced with zinc and acetic acid, yields 3-methyl-2-hydrindone, which melts at 62—63°. The *semicarbazone* melts at 195°. G. Y.

Tetrahydro- and Octohydro-anthracenes. MARCEL GODCHOT (*Compt. rend.*, 1904, **139**, 604—606).—*Tetrahydroanthracene*, $C_{14}H_{14}$, obtained by the hydrogenation of anthracene by the method of Sabatier and Senderens (compare Abstr., 1900, i, 469, 470, 471; 1901, i, 195) at a temperature of 250°, forms colourless crystals melting at 89° and boiling at 309—313°, is insoluble in water, slightly soluble in warm alcohol or acetic acid, more readily so in boiling benzene, the solutions exhibiting a strong blue fluorescence; it yields anthraquinone on oxidation and 9 : 10-dichloro- and 9 : 10-dibromo-anthracenes on treatment with chlorine or bromine.

Octohydroanthracene, $C_{14}H_{18}$, prepared by the direct hydrogenation of anthracene at 200°, of anthraquinone at 250°, or of tetrahydroanthracene at 190°, crystallises in colourless plates melting and subliming at 71° and boiling at 292—295°, is insoluble in water, and soluble in warm alcohol, acetic acid, or benzene and its homologues, the solutions possessing a characteristic green fluorescence. The *picrate*, $2C_{14}H_{18},C_6H_3O_7N_3$, melts at 80°. *Dibromo-octohydroanthracene*, $C_{14}H_{16}Br_2$,

crystallises in large, colourless needles melting at 194° (corr.), and is soluble in hot ethyl acetate, benzene, or chloroform, less readily so in alcohol or acetic acid, and the solutions are not fluorescent. *Dibromohexahydroanthracene*, $C_{14}H_{14}Br_2$, crystallises in thin, yellow needles melting at 162° (corr.) and exhibits a fine blue fluorescence in solution. *Bromo-octohydroanthracene*, $C_{14}H_{17}Br$, is a yellow liquid, readily soluble in the ordinary solvents, and loses HBr on distillation, forming a hydrocarbon not yet described. *Dichloro-octohydroanthracene*, $C_{14}H_{16}Cl_2$, melts at 192° (corr.), *dichlorohexahydroanthracene* melts at 159° (corr.), *chloro-octohydroanthracene*, $C_{14}H_{17}Cl$, is a liquid. M. A. W.

Formation of Phenanthrene from Fluorene. CARL GRAEBE (*Ber.*, 1904, **37**, 4145—4146).—On passing either ethyl- or methylfluorene through a glass tube heated to a faint red glow, phenanthrene is formed in considerable quantity. When 9-ethylfluorene is heated with lead oxide, reaction sets in at about 300°, and a *hydrocarbon* is formed, melting at 99—100°, and yielding a characteristic *picrate*, which melts at 156°. This is perhaps 9-methylphenanthrene.

E. F. A.

Triphenylmethyl. X. MOSES GOMBERG and L. H. CONE (*Ber.*, 1904, **37**, 3538—3547. Compare Abstr., 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244; this vol., i, 658).—The formation of triphenylmethyl peroxide by the action of oxygen on triphenylmethyl is accompanied by a development of heat. The yield of peroxide is 63—69·5 per cent. of the theoretical, or 80·3—86·6 if air is used instead of oxygen; about 20 per cent. of the peroxide formed decomposes immediately to oily products which are soluble in ether and contain about the same amount of oxygen as the peroxide.

Triphenylmethyl sulphate, $(CPh_3)_2SO_4$, formed by the action of silver sulphate on triphenylmethyl chloride, is dark red, forms intensely red solutions, has the conductivity $\mu_{10} = 49$ when dissolved in liquid sulphur dioxide, and is hydrolysed by moisture to triphenylcarbinol and sulphuric acid.

The action of bromine on triphenylmethyl peroxide in chloroform solution leads to the formation of *triphenylbromomethane pentabromide*, $C_{19}H_{15}Br,Br_5$, which is an unstable, dark red, crystalline substance. In carbon tetrachloride solution, the action of bromine on the peroxide leads to the formation of triphenylmethyl bromide. Triphenylbromomethane pentaiodide is formed by the action of bromine and an excess of iodine on the peroxide in chloroform solution. In boiling carbon tetrachloride solution in presence of iodine, the peroxide reacts with chlorine to form triphenylmethyl chloride, benzophenone chloride, and a substance which melts at 66—67° and is probably 2 : 4′-dichlorobenzophenone. The action of phosphorus pentachloride on the peroxide leads to the formation of benzophenone chloride and phenyldiphenylenemethane, which melts at 144°.

Whilst triphenylmethyl solutions undergo only slight decomposition when exposed to diffuse light, even after a year, a 15 per cent. solution in benzene is completely decolorised by exposure to direct sun-

light for 3—4 hours; the reaction takes place more rapidly in carbon tetrachloride, more slowly in carbon disulphide solution. The distillation residue from the benzene solution consists of triphenylmethane (65 per cent.), products insoluble in ether (25 per cent.), and an oil with a strong aromatic odour. The products insoluble in ether are an unsaturated substance which melts at about 237° and a saturated substance which melts at 194°. The distillation residue from the carbon tetrachloride solution consists of 50 per cent. of an oil and a mixture of crystalline substances, but no triphenylmethane.

The analogues of triphenylmethyl are still more sensitive to light.

G. Y.

The Triboluminescent Parent Hydrocarbon of Rosaniline. AUGUSTIN BISTRZYCKI and JOSEPH GYR (*Ber.*, 1904, **37**, 3696—3699. Compare this vol., i, 498, and E. and O. Fischer, *ibid.*, 863).—Careful comparisons of the hydrocarbons obtained by the authors, by E. and O. Fischer, and by Hemilian have established their identity. The latter gives a yellow coloration when rubbed with concentrated sulphuric acid, but this is probably due to a small amount of impurity. All three specimens exhibit triboluminescence. Diphenyl-*p*-tolylmethane, the corresponding ortho-compound, and diphenyl-*m*-tolylcarbinol do not show this property.

J. J. S.

Alkylated Aminoacetonitriles. EMIL KNOEVENAGEL (*Ber.*, 1904, **37**, 4073—4087)—[With KARL SCHLEUSSNER].—Anilinophenylacetonitrile is best prepared by warming mandelonitrile with aniline and potassium cyanide or sodium acetate in alcoholic solution. *p*-Toluidinophenylacetonitrile is obtained by a similar method. *o*-Toluidine does not react with mandelonitrile in presence of potassium cyanide at 100°. α-Naphthylaminophenylacetonitrile, prepared from mandelonitrile and α-naphthylamine in presence of potassium cyanide, melts at 106° (Sachs and Goldmann, Abstr., 1902, i, 780).

[With OTTO KLUCKE.]—When shaken with aqueous sulphurous acid, benzylideneaniline forms aniline anilinophenylmethanesulphonic acid, $NHPh\cdot CHPh\cdot SO_3H,NH_2Ph$, which crystallises in matted, white needles, melts at 124—125°, and is probably identical with Eibner's substance obtained from benzylideneaniline and sulphur dioxide in ethereal solution (Abstr., 1901, i, 378. Compare Speroni, Abstr., 1903, i, 246).

When warmed with potassium cyanide, the aqueous solution of sodium anilinomethanesulphonate, obtained by the action of aniline on formaldehyde dissolved in aqueous sulphurous acid, yields *anilinoacetonitrile*, which melts at 48°. The following substances have been prepared by this method: p-*toluidinoacetonitrile*, which melts at 57°; m-*xylidinoacetonitrile*, which melts at 50—52°; *α-naphthylaminoacetonitrile*, which melts at 44—45°; *β-naphthylaminoacetonitrile*, which melts at 82—85°; o-*carboxyphenylaminoacetonitrile*, which melts and decomposes at 182—184°; o-*chloroanilinoacetonitrile*, which boils at 174—175° under 15 mm. pressure, and when hydrolysed yields an *acid*, $C_8H_8O_2NCl$, which melts at 166—167° and loses CO_2 at 210°.

Piperidinoacetonitrile, $C_7H_{12}N_2$, is obtained by the action of potassium

cyanide on the aqueous solution of *sodium piperidinomethanesulphonate*, formed by the action of piperidine on formaldehyde in aqueous sulphurous acid solution. It is identical with Klages and Margolinsky's compound (this vol., i, 145). In similar manner, methylanilinoacetonitrile is obtained from methylaniline; *ethylanilinoacetonitrile*, $NEtPh\cdot CH_2\cdot CN$, which melts at 21° and boils at 150—151° under 13 mm. pressure, from ethylaniline, and *phenylbenzylaminoacetonitrile*, which is a viscid oil, from benzylaniline.

Sodium anilinophenylmethanesulphonate, $NHPh\cdot CHPh\cdot SO_3Na$, obtained by warming benzylideneaniline with aqueous sodium hydrogen sulphite, decomposes with evolution of sulphur dioxide on acidification, and, when boiled with dilute alcoholic potassium cyanide, forms anilinophenylacetonitrile.

Anilino-o-*hydroxyphenylacetonitrile*, formed from salicylideneaniline, crystallises in yellow needles, melts at 113—114°, and is probably identical with Haarmann's compound from hydrogen cyanide, salicylaldehyde, and aniline (*Ber.*, 1873, 6, 339). Anilino-*p*-*iso*propylphenylacetonitrile (cumenylanilinoacetonitrile, Miller and Plöchl, Abstr., 1899, i, 127) is obtained from cuminaldehyde and aniline. *Anilino*-p-*methoxyphenylacetonitrile* crystallises in white needles and melts at 104—105°. Methylanilinophenylacetonitrile, $NMePh\cdot CHPh\cdot CN$, obtained from methylaniline and benzaldehyde, is identical with Sachs and Goldmann's product from mandelonitrile (*loc. cit.*). *a-Piperidinopropionitrile*, $C_8H_{14}N_2$, is an oil and boils at 93—94° under 12·5 mm. pressure; *a-piperidinophenylacetonitrile* melts at 62—63°; *a-piperidino*-o-*hydroxyphenylacetonitrile* melts at 89—90°; *a-piperidino*-p-*methoxyphenylacetonitrile* melts at 75—76°; a-piperidinostyrylacetonitrile, from cinnamaldehyde, melts at 98—99°. G. Y.

Anilide and Phenetidide of Acetylglycollic Acid and of Acetylsalicylic Acid. Richard Anschütz and W. Bertram (*Ber.*, 1904, 37, 3975—3977).—*Acetylglycollylanilide* separates from water in silky needles and melts at 89—90°. *Acetylglycollylphenetidide* separates from dilute alcohol in glistening needles and melts at 130—131°. Acetylglycollic acid is readily hydrolysed by water.

Acetylsalicylylanilide separates from alcohol in glistening needles and melts at 136—137°. Acetylsalicylylphenetidide separates from alcohol in glistening needles and melts at 132°.

The compounds described differ from the acids from which they are derived in not being hydrolysed when boiled with water.

The pharmacological action of the various compounds was examined. A. McK.

Anilides of Oxalic Acid containing Sulphur and their Transformation Products. Arnold Reissert (*Ber.*, 1904, 37, 3708—3733).—The action of phosphorus pentasulphide on oxanilic acid, either alone or dissolved in boiling toluene or xylene, always gives rise to resinous products, but on adding the sulphide to ethyl oxanilate dissolved in boiling xylene, *ethyl thionoxanilate*, $NHPh\cdot CS\cdot CO_2Et$, is obtained, with a good yield, in the form of an oil; the crude ester is purified with difficulty, and is best converted directly into *thionoxanilic acid*, $NHPh\cdot CS\cdot CO_2H$, which crystallises from

water in bright yellow needles, melts at 101—102°, and gives a *sodium* salt, crystallising in bright yellow leaflets; the *calcium* salt forms needles. The *aniline* salt, $C_{14}H_{14}O_2N_2S$, crystallises in very slender needles and melts and decomposes at 155°, giving rise to a mixture of thioformanilide and diphenylformamidine.

When phosphorus pentasulphide is added to a boiling solution of phenyloxamide in xylene, a mixture of *phenylthionoxamide* and *phenyldithionoxamide* is obtained; the former, $NHPh\cdot CO\cdot CS\cdot NH_2$, crystallises from alcohol in short, thick, straw-coloured prisms and melts at 176°, whilst the latter, $NHPh\cdot CS\cdot CS\cdot NH_2$, crystallises from light petroleum in bright red needles and melts at 98°. On adding potassium ferricyanide to phenyldithionoxamide dissolved in 2½ per cent. aqueous sodium hydroxide, *thionoxanilonitrile*, $NHPh\cdot CS\cdot CN$, is obtained; it is purified by repeatedly dissolving it in aqueous sodium carbonate and precipitating with hydrochloric acid, and forms orange-yellow, woolly needles and melts at 82°. *Thionoxanilamide*, $NHPh\cdot CS\cdot CO\cdot NH_2$, is also formed in this case, but it is best obtained by warming the nitrile with dilute sodium hydroxide solution; it crystallises from alcohol in thick, yellow needles and melts at 169—170°.

When to oxanilide suspended in boiling xylene, phosphorus pentasulphide is added, a mixture of *thionoxanilide*, $NHPh\cdot CS\cdot CO\cdot NHPh$, and *dithionoxanilide*, $C_2S_2(NHPh)_2$, is obtained; the former crystallises from glacial acetic acid in long, thick, yellow needles melting at 144—145°, and the latter forms red or yellow needles according to the nature of the solvent and the concentration of the solution, and gives a colourless, hygroscopic *sodium* salt. *Thionoxanilidesulphonic acid*, $NHPh\cdot CS\cdot CO\cdot NH\cdot C_6H_4\cdot SO_3H$, obtained by dissolving thionoxanilide in cold concentrated sulphuric acid, gives a *sodium* salt, crystallising in bright yellow leaflets and dissolving in aqueous sodium hydroxide to form, probably, a *disodium* salt, $NPh:C(SNa)\cdot CO\cdot NH\cdot C_6H_4\cdot SO_3Na$; the structure of the acid follows from its giving anilinesulphonic acid and thionoxanilic acid when boiled with sodium hydroxide solution.

Phenylthionoxamide, $NHPh\cdot CO\cdot CS\cdot NH_2$, by analogy with Sandmeyer's synthesis of indigotin (Abstr., 1903, i, 486), should be convertible, when heated with sulphuric acid, into isatin; but practically the yield is very small. A better result is obtained by the similar treatment of thionoxanilide, when 25 per cent. of the theoretical quantity of isatin is formed.

When thionoxanilide is oxidised by heating it with concentrated or fuming sulphuric acid, *benzothiazolecarboxylic thionanilide*,

$$C_6H_4<{S \atop N}>C\cdot CS\cdot NHPh,$$

is obtained; it crystallises from glacial acetic acid in soft, golden needles and melts at 155°. When an excess of fuming sulphuric acid (20 per cent. anhydride) is used and the heating prolonged, the *sulphonic acid*, $C_6H_4<{S \atop N}>C\cdot CS\cdot NH\cdot C_6H_4\cdot SO_3H$, of the anilide is obtained; the *sodium* salt crystallises from water in leaflets with a bronze-like lustre. *Benzothiazolecarboxylic anilide*,

$$C_6H_4<{S \atop N}>C\cdot CO\cdot NHPh,$$

obtained by oxidising the corresponding thionanilide with alkaline potassium permanganate or by heating benzothiazolecarboxylic acid with aniline at 140—160°, crystallises from alcohol in yellow prisms or white needles and melts at 160°; its *sulphonic acid*, $C_6H_4<^S_N>C\cdot CO\cdot NH\cdot C_6H_4\cdot SO_3H$, was prepared similarly by oxidising the sulphonic acid of the thioanilide.

Thionoxanilic acid, probably reacting in the form $NPh:C(HS)\cdot CO_2H$, is readily oxidised by potassium ferricyanide in presence of aqueous sodium hydroxide, forming benzothiazolecarboxylic acid,

$$C_6H_4<^S_N>C\cdot CO_2H$$

(Hofmann, Abstr., 1887, 1040), the sparingly soluble *sodium* salt of which is very characteristic; the *ethyl* ester, $C_{10}H_9O_2SN$, crystallises from dilute alcohol or light petroleum in voluminous, white needles, melts at 70—71°, and is converted by alcoholic ammonia at 100° into the *amide*, $C_6H_4<^S_N>C\cdot CO\cdot NH_2$, which crystallises from acetic acid on adding water, melts at 228—230°, and is also obtained by oxidising thionoxanilic amide with an excess of potassium ferricyanide.

W. A. D.

Isomerism of Asymmetric Tolylammonium Salts. II. EDGAR WEDEKIND and F. OBERHEIDE (*Ber.*, 1904, **37**, 3894—3898. Compare this vol., i, 732).—*Allyl*-o-*toluidine*, prepared by the action of allyl iodide on sodium formotoluidide and subsequent hydrolysis, and purified by conversion into its nitroso-derivative, is a yellow oil boiling at 225—230°. Benzyl iodide reacts vigorously with it, forming *benzylallyl*-o-*toluidine*, a yellow oil, boiling at 180—183° under 27 mm. pressure. The *picrate* forms lemon-yellow needles and melts at 148—150°. The base combines with methyl iodide, forming *benzyl*-o-*tolylmethylallylammonium iodide*, which separates from alcohol in colourless crystals and melts and decomposes at 154—155°.

Methylallyl-o-*toluidine*, obtained from methyl-*o*-toluidine and allyl iodide, distils at 215—220°. The *picrate* crystallises in lemon-yellow needles and melts at 133—135°. The tertiary base combines with benzyl iodide, yielding the quaternary ammonium iodide, which could only be obtained in an amorphous form.

Benzylmethyl-*o*-toluidine boils at 167° under 13 mm. pressure (compare Rabaut, Abstr., 1892, 313). The *picrate* forms thick, yellow needles melting at 127—128°. The base reacts with difficulty with allyl iodide, and only traces of an amorphous ammonium iodide are obtained.

C. H. D.

Benzylmalimides. ALBERT LADENBURG and WALTER HERZ (*J. pr. Chem.*, 1904, [ii], **70**, 342—344).—A reply to Lutz (this vol., i, 831).

G. Y.

Benzylethylaniline. GUSTAV SCHULTZ, G. ROHDE, and EBERHARD BOSCH (*Annalen*, 1904, **334**, 235—264. Compare Abstr., 1902, i, 364).—*Benzylethylaniline picrate* melts at 116—117°; *benzylethyl-*

aniline methiodide crystallises in prisms and melts and decomposes at 140·5°. *Benzylethyl*-p-*nitrosoaniline*, $ON{\cdot}C_6H_4{\cdot}NEt{\cdot}CH_2Ph$, prepared by a method analogous to that used for *p*-nitrosodimethylaniline, forms steel-blue crystals, melts at 61—62°, and yields benzaldehyde when boiled with concentrated hydrochloric acid. Its *hydrochloride* crystallises in yellow leaflets and melts and decomposes at 116°; it readily undergoes hydrolytic dissociation.

When benzylethylaniline is nitrated, a mixture of two mononitro-derivatives, where the substitution of the nitro-groups occurs in the benzyl residue, is produced. The main product is m-*nitrobenzylethylaniline*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NEtPh$, which separates from alcohol in reddish-brown prisms and melts at 69°; its *hydrochloride* forms snow-white prisms and melts at 186°, whilst its *picrate* melts at 131°. When *m*-nitrobenzylethylaniline is oxidised in acetic acid solution by chromic acid, it forms *m*-nitrobenzoic acid. Its constitution was further proved by its synthesis from *m*-nitrobenzylchloride and ethylaniline. p-*Nitrobenzylethylaniline* forms yellow, rhombic crystals and melts at 67°; its constitution was proved by its synthesis from *p*-nitrobenzyl chloride and ethylaniline. o-*Nitrobenzylethylaniline*, prepared from *o*-nitrobenzyl chloride and ethylaniline, forms brown, rhombic crystals and melts at 66°; its *hydrochloride* melts at about 158°; its *platinichloride* melts and decomposes at 116—117°.

Attempts were made to replace the bromine atom in bromonitrobenzene by the benzylethylamine group. Benzylethylamine (2 mols.) was heated with *o*-bromonitrobenzene (1 mol.) and alcohol for 5 hours at 150°, the product made alkaline with sodium hydroxide and the excess of amine removed by steam distillation, when the residue yielded *benzylethyl*-o-*nitroaniline*,

$$NO_2{\cdot}C_6H_4{\cdot}NEt{\cdot}CH_2Ph,$$

as a yellow oil; its *platinichloride*, which melts and decomposes at 176·5°, is not decomposed by water and alcohol, differing in this respect from the platinichloride of the isomeric *o*-nitrobenzyl compound previously described.

Experiments to replace the hydrogen in the amino-group of *m*- and *p*-nitroethylanilines by the benzyl group gave negative results. It was also not found possible to oxidise benzylethyl-*p*-nitrosoaniline to benzylethyl-*p*-nitroaniline by means of potassium permanganate, lead peroxide, potassium persulphate, hydrogen peroxide, ferric chloride, and nitrous acid respectively. *Dinitrobenzylethylaniline*, $C_{15}H_{15}O_4N_3$, prepared by the action of dilute nitric acid on a solution of benzylethyl-*p*-nitrosoaniline in glacial acetic acid, or by the nitration of benzylethylaniline with fuming nitric acid, separates from alcohol in dark yellow, rhombic crystals and melts at 71°. *Benzylethyl*-p-*nitroaniline*, $NO_2{\cdot}C_6H_4{\cdot}NEt{\cdot}CH_2Ph$, prepared by nitrating a solution of benzylethylaniline in glacial acetic acid by fuming nitric acid, separates from alcohol in dark yellow crystals with blue lustre and melts at 63°. Like dibenzyl-*p*-nitroaniline it does not exhibit basic properties.

Reduction of those mononitrobenzylethylanilines where the nitro-group is substituted in the benzyl group could not be effected.

as-Benzylethyl-p-phenylenediamine, $NH_2 \cdot C_6H_4 \cdot NEt \cdot CH_2Ph$, prepared by reducing benzylethyl-*p*-nitrosoaniline with zinc dust and sulphuric acid, is a colourless, viscid oil, which boils at 225° under 21 mm. pressure. The *oxalate* crystallises from water in needles and melts at 168—169°; the *benzoyl* derivative crystallises in needles and melts at 131·5°; the *acetyl* derivative crystallises in needles and melts at 111°.

When an aqueous solution of hydrogen sulphide and then a few drops of ferric chloride are added to a solution of *as*-benzylethyl-*p*-phenylenediamine hydrochloride, a blue coloration appears, owing to the formation of a thiazine dye analogous to methylene-blue.

Benzylethylanilinophenylthiocarbamide melts at 149°. The *azo-dye*, produced by coupling diazotised *as*-benzylethyl-*p*-phenylenediamine with an alkaline solution of β-naphthol, separates from acetone or ethyl acetate in black crystals with a green lustre and melts at 135·5°. A. McK.

Acylaminomethanesulphonic Salts and their Behaviour towards Potassium Cyanide. EMIL KNOEVENAGEL and HANS LEBACH (*Ber.*, 1904, 37, 4094—4104. Compare this vol., i, 983, 989).—The amides of aromatic carboxylic and sulphonic acids react with formaldehyde and sodium hydrogen sulphite to form sodium acylaminomethanesulphonates. Those derived from sulphonamides react with potassium cyanide to form the corresponding nitriles.

Sodium benzoylaminomethanesulphonate, $NHBz \cdot CH_2 \cdot SO_3Na$, decomposes without melting when heated above 220°, is easily soluble in water, but only slightly so in alcohol. The *barium* and *lead* salts are insoluble in water, the *silver* salt forms a red precipitate which gradually blackens.

The action of phosphorus pentachloride on the sodium salt under dry ether at 40—50° leads to the formation of *s*-dibenzoyldiaminomethane; if the action takes place in absence of a solvent and the product is distilled or treated with ice-water there is obtained a solid *substance* which melts under warm water and is probably a chloro-derivative of *s*-dibenzoyldiaminomethane.

Sodium anisylaminomethanesulphonate,

$$OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot SO_3Na,$$

crystallises in colourless needles containing $1H_2O$, which is lost at 105°. When treated with phosphorus oxychloride in ethereal solution under reduced pressure, it yields *methylenedianisamide*,

$$CH_2(NH \cdot CO \cdot C_6H_4 \cdot OMe)_2,$$

which is also formed from N-methylolanisamide, separates from alcohol in white crystals, and melts at 206—207·5°.

Sodium benzenesulphonylaminomethanesulphonate,

$$SO_2Ph \cdot NH \cdot CH_2 \cdot SO_3Na,$$

forms an amorphous, white mass and decomposes above 110° with evolution of formaldehyde; it reacts violently with phosphorus pentachloride, but no substance resembling hipparaffin could be obtained. *Benzenesulphonylaminoacetonitrile*, $SO_2Ph \cdot NH \cdot CH_2 \cdot CN$, crystallises in long, colourless, glistening needles and melts at 76—77°; the *potassium* derivative, $SO_2Ph \cdot NK \cdot CH_2 \cdot CN$, crystallises in colourless

needles. When evaporated with concentrated hydrochloric acid, the nitrile yields *benzenesulphonylaminoacetic acid*, which crystallises in colourless needles and melts at 165—166°.

Sodium benzene-m-*disulphonylaminomethanesulphonate*,

$$C_6H_4(SO_2\cdot NH\cdot CH_2\cdot SO_3Na)_2,$$

crystallises in small needles.

Benzene-m-*disulphonylaminoacetonitrile* crystallises in glistening needles and melts at 149—150°. The acid melts and decomposes at 181°; the *ammonium*, *sodium*, *barium*, *calcium*, *magnesium*, *lead*, *copper*, and *zinc* salts are described. The *ethyl* ester,

$$C_6H_4(SO_2\cdot NH\cdot CH_2\cdot CO_2Et)_2,$$

crystallises in glistening needles and melts at 110°.

Methylenebenzene-m-*disulphonamide*, $C_6H_4<\begin{matrix}SO_2\cdot NH\\SO_2\cdot NH\end{matrix}>CH_2$, or

$$NH_2\cdot SO_2\cdot C_6H_4\cdot SO_2\cdot N:CH_2,$$

formed by the action of formaldehyde on benzene-*m*-disulphonamide, is amorphous, decomposes when heated above 180°, is easily soluble in aqueous alkali hydroxides, and forms a *potassium* derivative crystallising in needles (compare Magnus-Levy, Abstr., 1893, i, 714).

G. Y.

Condensation Products of ψ-Phenols with Dimethylaniline and Analogous Tertiary Bases. KARL AUWERS (*Annalen*, 1904, **334**, 264—342. Compare Abstr., 1902, i, 146; 1903, i, 621; this vol., i, 487).—The author has previously shown that primary or secondary bases react with ψ-phenols to form secondary or tertiary amines, the primary base forming a tertiary amine with two aromatic rings. The action of tertiary bases on ψ-phenols is different; with aliphatic tertiary amines, halogen hydride is eliminated, whilst Zincke's methylenequinones are probably formed and undergo immediate polymerisation; tertiary cyclic bases, on the other hand, such as pyridine and quinoline, combine with ψ-phenols to form ammonium salts, the bases corresponding with which are very unstable and yield derivatives of diphenylmethane which do not contain nitrogen.

The condensation products, obtained by the action of dimethylaniline on ψ-phenols, are not salts of quaternary bases, since, by the action of alkali hydroxides, halogen hydride is readily eliminated, whilst compounds are produced having both phenolic and basic characters from which the original condensation product may be regenerated by the action of halogen hydride. Arguments are adduced in favour of those condensation products being regarded as derivatives of diphenylmethane, special reference being made to the constitution of the compound obtained from dimethylaniline and dibromo-*p*-hydroxy-ψ-cumyl bromide.

The action of *as*-dimethyl-*p*-phenylenediamine on dibromo-*p*-hydroxy-ψ-cumyl bromide was studied with the view of finding whether the former acts as a primary or a tertiary amine, and in this way elucidating the nature of the condensation product. It acts exclusively as a tertiary amine, the condensation product yielding, on treatment with acetic anhydride, a monoacetyl derivative, which may also be obtained by the action of the ψ-phenol on acetyl-*as*-dimethyl-*p*-phenylenediamine.

In the condensations under consideration, the halogen hydride salts of dimethylaminodiphenylmethane are first formed and they are converted into the free bases by means of alkali. When the methiodides of those condensation bases are boiled with xylene or acetic anhydride, methyl iodide is eliminated. The insolubility of the bases in aqueous alkali hydroxides is due to the influence of the strongly positive substituents, which mask the slightly acid nature of the phenolic group.

The action of bromine on derivatives of diethylaniline as contrasted with its action on derivatives of dimethylaniline is discussed.

The condensation of dimethylaniline has been studied only in the cases of those ψ-phenols where the negative reactive substituent is a halogen atom, so that it is uncertain whether the formation of diphenylmethane derivatives is general.

[With R. JACOB.]—Experiments were conducted to find out whether the condensation product of dibromo-*p*-hydroxy-ψ-cumyl bromide with dimethylamine was of phenolic or of betaine nature, and whether a double linking was present in its molecule.

3 : 6-Dibromo-4′- dimethylamino - 4 - hydroxy - 2 : 5-dimethyldiphenylmethane (compare Auwers and Avery, Abstr., 1896, i, 150), when heated with acetyl chloride at 150°, forms the *acetyl* derivative,

$$NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6Me_2Br_2 \cdot OAc,$$

which separates from alcohol in glistening, flat needles, melts at 144—145°, and forms a *hydrochloride* separating from benzene in needles and melting at 270—273°. The *methiodide* of the acetyl derivative separates from a mixture of chloroform and light petroleum and melts at 169—171°. When the methiodide of the free base is acetylated, the acetate of the base is formed.

3 : 6-Dibromo-4-hydroxy-2 : 5-dimethyldiphenylmethane-4′-trimethylammonium hydroxide, $OH \cdot NMe_3 \cdot C_6H_4 \cdot CH_2 \cdot C_6Me_2Br_2 \cdot OH$ (compare Auwers and Senter, Abstr., 1896, i, 423), prepared by the action of dilute sodium hydroxide on the methiodide of the corresponding amine, crystallises from dilute alcohol in prismatic pyramids and melts at 208°. Its *nitrate* forms transparent, glistening needles and melts and decomposes at 212—214°; its *hydrochloride* forms transparent, tiny neeedles and melts at 225—226°; its *hydriodide* separates from a mixture of chloroform and light petroleum in rhombic crystals, melts at 190—191°, and is not decomposed when boiled with water. When the methiodide is boiled with xylene, a substance, crystallising partly in needles and partly in prisms, is obtained, which melts at 124° and is identical with the base obtained from dimethylaniline and ψ-cumenol tribromide.

3 : 6-Dibromo - 4 - hydroxy - 2 : 5 - dimethyldiphenylmethane - 4 ′- trimethylammonium hydroxide, when acted on by acetic anhydride in the cold, forms transparent leaflets of a *compound* melting at 65—66°, which is probably the acetate of the acetyl derivative. The corresponding *hydrochloride*, $C_{20}H_{24}O_2NClBr_2$, forms white crystals and melts at 205—207°; by the action of moist silver oxide, it forms the *acetyl* derivative of 3 : 6-*dibromo*-4-*hydroxy*-2 : 5-*dimethyldiphenylmethane*-4′-*trimethylammonium hydroxide*, $OH \cdot NMe_3 \cdot C_6H_4 \cdot CH_2 \cdot C_6Me_2Br_2 \cdot OAc$, which crystallises in yellow, hygroscopic leaflets, softening at 95° and decomposing at 120°.

3 : 6 : 3′-*Tribromo-4′-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane hydrobromide*, prepared by adding bromine to a solution of 3 : 6-dibromo-4′-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane in glacial acetic acid, separates from glacial acetic acid in glistening needles and leaflets and melts at 204°. When boiled with water, it loses hydrogen bromide and forms the free *base*,

$$NMe_2\cdot C_6H_3Br\cdot CH_2\cdot C_6Me_2Br_2\cdot OH,$$

which separates from alcohol in tiny needles and melts at 99—100°. When excess of hydrobromic acid is added to a hot solution of the base in sodium hydroxide, the hydrobromide is again formed. The *acetyl* derivative of the base forms leaflets of a silvery lustre and melts at 156—157°.

[With JOH. REICHEL.]—The incorrectness of the betaine structure, which was originally assigned to the condensation bases, is further shown by the following results.

The methoxyl group in the side-chain of dibromo-*p*-hydroxy-ψ-cumylalcohol dimethyl ether (compare Auwers and Baum, Abstr., 1897, i, 34) is readily replaced by iodine by the action of hydriodic acid on the ether at the ordinary temperature; the replacement by bromine takes place by the action of hydrobromic acid at 100°, whilst the replacement by chlorine is effected when hydrogen chloride is passed for a long time into a concentrated boiling solution of the ether in acetic acid.

Dibromo-p-*hydroxy-ψ-cumyl chloride methyl ether*,

$$CH_2Cl\cdot C{<}{\genfrac{}{}{0pt}{}{CMe{:}CBr}{CBr\cdot CMe}}{>}C\cdot OMe,$$

separates from glacial acetic acid in glistening needles and melts at 116—117°. *Dibromo*-p-*hydroxy-ψ-cumyl bromide methyl ether* separates from glacial acetic acid in glistening needles and melts at 122—124°. *Dibromo*-p-*hydroxy-ψ-cumyl iodide methyl ether* melts at 114—115°.

Dibromo-p-*hydroxy-ψ-cumylaniline methyl ether*,

$$NHPh\cdot CH_2\cdot C{<}{\genfrac{}{}{0pt}{}{CMe{:}CBr}{CBr\cdot CMe}}{>}C\cdot OMe,$$

prepared by the addition of aniline to a benzene solution of the preceding iodide, separates from alcohol in glassy needles and melts at 115—116°. The corresponding *piperidine* derivative, $C_{15}H_{21}ONBr_2$, separates from alcohol in glassy plates and melts at 49—51°. *Dibromo*-p-*hydroxy-ψ-cumylmethylaniline methyl ether*, prepared from the iodide and monomethylaniline, forms colourless prisms and melts at 90—91°.

Dibromo-p-*acetoxy-ψ-cumylmethylaniline*, prepared from dibromo-*p*-acetoxy-ψ-cumyl bromide and methylaniline, separates from methyl alcohol in prisms and melts at 102—103°.

When either of the two latter compounds is boiled for 8 hours with an excess of methyl iodide and benzene at 100° in the presence of a little mercury, phenyltrimethylammonium iodide is produced.

When dimethylaniline is condensed with dibromo-*p*-hydroxy-ψ-cumyl iodide at the ordinary temperature, the *hydriodide*,

$$HI,NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6Me_2Br_2\cdot OH,$$

is formed; it crystallises in leaflets of a mother-of-pearl lustre and melts at 220°.

[With O. WEHR.]—p-*Hydroxyphenyltrimethylammonium iodide*,

$$OH\cdot C_6H_4\cdot NMe_3I,H_2O,$$

prepared by the action of methyl iodide and a concentrated aqueous solution of potassium hydroxide on a solution of *p*-aminophenol hydrochloride in methyl alcohol, melts at temperatures varying between 190° and 201° according to the rapidity of heating; it forms yellow plates. When heated with acetic anhydride in presence of carbon dioxide, it is converted into *acetyl-p-dimethylaminophenol*, $OAc{\cdot}C_6H_4{\cdot}NMe_2$, which crystallises from dilute alcohol in needles or plates and melts at 78—79°. When the latter compound is heated with alcoholic potassium hydroxide, *p*-dimethylaminophenol is produced. *Acetyl-p-dimethylaminophenol methiodide*, $C_{11}H_{16}O_2NI$, melts at 192—193°.

[With O. WEHR.]—Monoacetyl-*as*-dimethyl-*p*-phenylenediamine is formed when *p*-aminodimethylaniline is mixed with a slight excess of acetic anhydride at the ordinary temperature; when heated with an excess of acetic anhydride, it forms *diacetyl-p-aminodimethylaniline*, which separates from light petroleum in needles and melts at 68—69°; it may also be prepared by heating the free base with an excess of acetic anhydride.

3 : 6-*Dibromo-5'-amino-2'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane hydrobromide*,

$$NH_2{\cdot}C_6H_3(NMe_2){\cdot}CH_2{\cdot}C_6Me_2Br_2{\cdot}OH,HBr,$$

prepared from dibromo-*p*-hydroxy-ψ-cumyl bromide and *p*-aminodimethylaniline, melts at 189—190°; the free *base* is a dirty yellow powder, melts at 141—142°, and forms a *monoacetyl* derivative, crystallising in glistening, yellow scales and melting at 223—224°; the *diacetyl* derivative separates from alcohol in yellow leaflets and melts at 138—139°.

3:6-*Dibromo-4'-dimethylamino-4-hydroxy-2:5-dimethyldiphenylmethane ethiodide*, $NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6Me_2Br_2{\cdot}OH,EtI$, is a yellowish-white, crystalline powder, which, when quickly heated, melts at 175—176° and, when slowly heated, at 172—173°. When boiled with an alkali hydroxide, it is converted into the *base*, $C_{19}H_{25}O_2NBr_2$, which crystallises in white leaflets and melts at 189—190°.

Acetyl-3 : 6-dibromo-4'-diethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane, $NEt_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6Me_2Br_2{\cdot}OAc$, separates from alcohol in glistening scales and melts at 139—140°. Its *methiodide* forms white leaflets and melts at 191—192°. When the free base is brominated, it forms 3 : 6 : 3'-*tribromo-4'-diethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane*, which does not crystallise and on exposure becomes tarry.

[With O. HÄHNLE.]—The following compounds were prepared to test whether the phenomena, which were first observed in the ψ-cumenol series, are general for ψ-phenols of the para-series.

If molecular amounts of dibromo-*p*-hydroxymesityl bromide and dimethylaniline are mixed in benzene solution, 2 : 6-*dibromo-4'-dimethylamino-4-hydroxy-3 : 5-dimethyldiphenylmethane hydrobromide*,

$$NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6Me_2Br_2{\cdot}OH,HBr,$$

is formed as silky needles, melting completely at 250°. The free *base* melts at 128°; its *acetate* separates from alcohol in white needles and melts at 145—146·5°; its *methiodide* separates from glacial acetic acid in yellow crystals, melts and decomposes at 193—196°, and forms an *acetyl* derivative which melts and decomposes at 184—185°. The

corresponding *quaternary base*, $OH \cdot NMe_3 \cdot C_6H_4 \cdot CH_2 \cdot C_6Me_2Br_2 \cdot OH$, prepared by the action of dilute sodium hydroxide on the iodide, forms leaflets or needles of a mother-of-pearl lustre, which soften at 160° and melt at 188—191°.

2 : 6 : 3′-*Tribromo-4′-dimethylamino-4-hydroxy-3 : 5-dimethyldiphenylmethane hydrobromide*, prepared by bromination of the base melting at 128°, separates from glacial acetic acid in grey leaflets of a fatty lustre and melts at 224—224·5°. The free *base* separates from dilute alcohol in pink needles and melts at 135°; its *acetyl* derivative separates from alcohol in glassy needles and melts at 150—151·5°; its *methiodide* forms yellow needles, melts and decomposes at 172—173°, and, when boiled with xylene, parts with methyl iodide.

The condensation of dibromo-*p*-hydroxymesityl bromide with diethylaniline proceeds similarly to that with dimethylaniline. 2 : 6-*Dibromo-4′-diethylamino-4-hydroxy-3 : 5-dimethyldiphenylmethane hydrobromide* forms silky needles and melts and decomposes at 278—279°. The free *base* separates from dilute alcohol in rhombic plates and melts completely at 132—133°.

[With R. Zaubitzer.]—Whilst *o*-ψ-phenols condense with dimethylaniline quite as readily as do *p*-ψ-phenols, dibromo-*m*-hydroxy-ψ-cumyl bromide does not.

Tetrabromo-*o*-hydroxybenzyl bromide interacts with dimethylaniline to form the *hydrobromide*, $C_{15}H_{14}ONBr_5$, which forms silky needles and melts at 213—214°. The free *base*, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6Br_4 \cdot OH$, separates from a mixture of light petroleum and benzene in pyramids of a diamond lustre and melts at 121—123°; its *methiodide* forms golden-yellow needles and melts at 165—166°.

[With Wilhelm Strecker.]—*o-Bromo-*p*-hydroxybenzyl alcohol*, prepared by the action of carbon dioxide on a mixture of *m*-bromophenol, sodium hydroxide, and formaldehyde which had remained at the ordinary temperature for 10 days, forms glistening needles and melts at 137—138°. When bromine is added to its solution in glacial acetic acid, tribromo-*p*-hydroxybenzyl bromide, melting at 122°, is produced (compare Zincke and Wiederhold, Abstr., 1902, i, 284). When the benzene solution of the latter compound is mixed with dimethylaniline, 2 : 3 : 5-*tribromo-4′-dimethylamino-4-hydroxydiphenylmethane hydrobromide*, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6HBr_3 \cdot OH,HBr$, is produced; it separates from glacial acetic acid in glistening leaflets and melts at 224—225°. The free *base* crystallises from alcohol in needles and melts at 127°; its *methiodide* forms a yellow, crystalline powder and melts at 171—173°.

When *p*-ethylphenol tetrabromide, $CHMeBr \cdot C {\lessdot}\begin{matrix} CBr{:}CBr \\ CH{-}CBr \end{matrix}{\gtrdot} C \cdot OH$, is condensed with dimethylaniline, it forms 2 : 3 : 5-*tribromo-4′-dimethylamino-4-hydroxy*-as-*diphenylethane hydrobromide*,

$$NMe_2 \cdot C_6H_4 \cdot CHMe \cdot C_6HBr_3(OH),HBr,$$

which melts at 202—207°. The free *base* crystallises from alcohol in needles and melts at 108°; its *hydriodide* forms glistening, yellow crystals and melts at 183—185°.

[With Wilhelm Strecker.]—By the partial reduction of 3 : 6-dibromo-4′-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane by

means of zinc dust and acetic acid, as well as by its reduction by sodium amalgam in alkaline solution, *6-bromo-4'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane*, $NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6HMe_2Br\cdot OH$, was produced; it separates from dilute alcohol in pink crystals and melts at 155—157°. When the reduction is conducted with sodium and boiling alcohol, *4'-dimethylamino-4-hydroxy-2 : 5-dimethyldiphenylmethane*, $NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_2Me_2(OH)$, was produced; this melts at 153—155°.

3 : 5-*Dibromo-4'-dimethylamino-4-hydroxydiphenylmethane hydrobromide*, $NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_2Br_2\cdot OH,HBr$, prepared from dimethylaniline and dibromo-*p*-hydroxybenzyl bromide, melts at 118—122°; the free *base* was not obtained pure, but its *methiodide* forms yellow leaflets and needles of a mother-of-pearl lustre and melts and decomposes at 175°.

When the condensation product formed from dibromo-*p*-hydroxybenzyl bromide and dimethylaniline is dissolved in alcohol, sodium added, and then carbon dioxide passed into the product, from which the alcohol had been removed, *4'-dimethylamino-4-hydroxydiphenylmethane*, $NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot OH$, is precipitated; it separates from light petroleum in glistening prisms and melts at 108—109°. Its *benzoyl* derivative forms glistening leaflets and melts at 118—118·5°. That the two latter compounds were derivatives of diphenylmethane was also proved by their preparation from 4-amino-4'-diphenylaminodiphénylmethane, obtained from *p*-dimethylaminobenzyl-*p*-toluidine.

A. McK.

Tetrachlorophenol and Pentachlorophenol. Heinrich Biltz and Wilhelm Giese (*Ber.*, 1904, **37**, 4010—4022. Compare this vol., i, 1021, 1022).—Tetrachlorophenol (Zincke and Schaum, Abstr., 1894, i, 231), obtained by reduction of α-heptachloroketotetrahydrobenzene with stannous chloride and hydrochloric acid in warm acetic acid solution, contains pentachlorophenol; the two may be separated by fractional distillation, as tetrachlorophenol boils at 150° and pentachlorophenol at 195° under 16 mm. pressure. If, during the reduction, the temperature of the reacting mixture is kept below 10°, tetrachlorophenol only is formed.

2 : 3 : 4 : 6-Tetrachlorophenol melts at 69—70° (Zincke and Walbaum, Abstr., 1891, 710, give the melting point as 67°) and boils at 155° under 18 mm., at 159° under 20 mm., and at 164° under 23 mm. pressure. Hugounenq's compound melting at 152° (Abstr., 1891, i, 297) was chiefly pentachlorophenol.

The *sodium* derivative, C_6HOCl_4Na, crystallises in clusters of white needles and melts at 370°; the acetate, $C_8H_4O_2Cl_4$, forms small, white crystals and melts at 65—66°; the methyl ether (Hugounenq, Abstr., 1890, 241) crystallises in colourless needles and melts at 64—65°; the *ethyl ether* crystallises in long needles and melts at 59—60°; the *phenylcarbamate*, $C_{13}H_6O_2Cl_4N$, crystallises in long, colourless needles and melts at 141—142°.

Trichloroquinone, obtained by the action of fuming nitric acid on tetrachlorophenol, melts at 169—170°; trichloroquinol is found to melt at 138°. The action of boiling bromine water on tetrachloro-

phenol leads to the formation of chloranil and oily products. With chlorine in anhydrous acetic acid, tetrachlorophenol yields heptachloroketotetrahydrobenzene.

Pentachlorophenol is best prepared by long boiling of heptachloroketotetrahydrobenzene in acetone solution. The *ethyl ether* crystallises in long, colourless prisms and melts at 89—90°; the n-*propyl ether* crystallises in colourless prisms and melts at 49—50°; the n-*butyl ether* melts at 15·5—16·5° and boils at about 343°; the *benzyl ether* crystallises in long prisms and melts at 167—168°; the *benzoate* crystallises in long, pointed prisms and melts at 164—165°. When chlorinated at the ordinary temperature, pentachlorophenol yields octachloroketotetrahydrobenzene (Zincke and Schaum, *loc. cit.*), but if chlorination takes place at 100° the product is a mixture of hexa- and octa-chloroketotetrahydrobenzenes (Barral, Abstr., 1895, i, 272). G. Y.

Electrolytic Preparation of *p*-Aminophenol. FRIEDRICH DARMSTÄDTER (D.R.-P. 154086).—In the preparation of *p*-aminophenol by the electrolytic reduction of nitrobenzene, the concentrated sulphuric acid may be advantageously replaced by 80 per cent. acid, the nitrobenzene being then in suspension, and not in solution. The diaphragms and other parts of the apparatus are thus less attacked, and the loss of acid by dilution is reduced. An excess of nitrobenzene must be present throughout in order to avoid reduction to aniline. A current density of 6 amperes per sq. dm. is suitable. The method is also applicable to derivatives of *p*-aminophenol. C. H. D.

Anethole Nitrosochloride. ERNST SCHMIDT and A. ADLUNG (*Chem. Centr.*, 1904, ii, 1038; from *Apoth.-Zeit.*, 19, 655—656).—The additive compounds of anethole, esdragole, eugenol, methyleugenol, *iso*eugenol, methyl*iso*eugenol, and asarone with nitrosyl chloride have been prepared and compared with the products obtained by Wallach's method of preparation by the action of amyl nitrite and hydrochloric acid. In the case of anethole, both methods yield the same nitrosochloride, $OMe\cdot C_6H_4\cdot C_3H_5\cdot NOCl$, melting at 127°; the piperidine compound, $OMe\cdot C_6H_4\cdot C_3H_5\cdot NO\cdot C_5NH_{10}$, melts at 107°. The difference of the behaviour of the propenyl and allyl groups towards nitrosyl chloride is similar to that of their behaviour with nitrogen trioxide, but some of the nitrites of the propenyl derivatives appear to be formed more readily than the nitrosochlorides. E. W. W.

Reduction of Unsaturated Phenol Ethers by Sodium and Alcohol. AUGUST KLAGES (*Ber.*, 1904, 37, 3987—4002. Compare this vol., i, 45).—*p*-Propylanisole, obtained by reduction of *p*-propenylanisole with sodium and alcohol, has a sp. gr. 0·94718 at 20°/4° and n_D 1·5045 at 20°.

2-Ethoxy-1-α-hydroxypropylbenzene, $OEt\cdot C_6H_4\cdot CHEt\cdot OH$, prepared by the action of magnesium ethyl iodide on salicylaldehyde ethyl ether, is a viscid, colourless oil, boils at 129—130° under 15 mm. pressure, and, when strongly cooled, solidifies to colourless crystals. The *phenyl-*

urethane, $C_{18}H_{21}O_3N$, crystallises in colourless needles and melts at 95—96°.

o-*Propenylphenetole*, $OEt\cdot C_6H_4\cdot CH\colon CHMe$, is obtained by converting 2-ethoxy-1-α-hydroxypropylbenzene into its *chloride* and heating with pyridine at 120°, and along with γ-*o*-ethoxyphenyl*iso*crotonic acid by heating salicylaldehyde ethyl ether with propionic anhydride and sodium propionate at 150°. It is a colourless oil, has a pleasant odour, boils at 120—121° under 17 mm., or at 230—231° under 757 mm. pressure, is volatile in a current of steam, and is reduced, by sodium and alcohol, to o-*propylphenetole*, $OEt\cdot C_6H_4Pr^{\alpha}$, which is a colourless, mobile liquid and boils at 99—100° under 16 mm. or at 213° under 754 mm. pressure.

γ-o-*Ethoxyphenyl*iso*crotonic acid*, $OEt\cdot C_6H_4\cdot CH\colon CH\cdot CH_2\cdot CO_2H$, crystallises from dilute alcohol, melts at 130—131°, and is not volatile in a current of steam; the *silver* salt, $C_{12}H_{13}O_3Ag$, is obtained as a white precipitate; the *methyl* ester is an oil. m-*Ethoxyphenyl*iso*crotonic acid*, formed, along with *m*-propenylphenetole, by the action of propionic anhydride and sodium propionate on *m*-ethoxybenzaldehyde at 150°, crystallises in colourless needles and melts at 98°; the *methyl* ester is a colourless, odourless oil and boils at 175—176° under 14 mm. pressure.

m-*Propenylphenetole*, which is obtained also by heating a mixture of *m*-ethoxybenzaldehyde and magnesium ethyl iodide on the water-bath for some hours, is a mobile oil, has a fruity odour, and boils at 124—125° under 16 mm. pressure; the *nitrosochloride* derivative melts at 122—123°. m-*Propylphenetole*, formed by reduction of *m*-propenylphenetole, is a colourless, mobile oil, boils at 109—110° under 15 mm., or at 220—224° under 753 mm. pressure, and, when treated with concentrated sulphuric acid, forms a *sulphonic acid*. The *barium sulphonate* crystallises in leaflets and is easily soluble in water; the *sulphonic chloride* is an oil; the *sulphonamide* crystallises in slender needles and melts at 84°.

p-*Propylphenetole*, obtained by reduction of *p*-propenylphenetole, is a colourless oil, has an odour resembling that of anise, boils at 108—110° under 13 mm. pressure, has a sp. gr. 0·9400 at 15°/4°, and, when cooled with carbon dioxide and ether, solidifies to a colourless, crystalline mass. The *sulphonic acid* crystallises in long, glistening needles and melts at 66—68°; the *barium* salt is easily soluble in water; the *sulphonamide* crystallises in colourless needles and melts at 97—98°.

4-*Propionyl-2-methylanisole*, $OMe\cdot C_6H_3Me\cdot CO\cdot CH_2Me$, formed by the action of propionyl chloride and aluminium chloride on *o*-tolyl methyl ether in light petroleum, solidifies to a crystalline mass, melts at 41°, and boils at 169—171° under 25 mm. pressure. The *oxime* crystallises as glistening leaflets, melts at 99°, and forms a *sodium* derivative as small needles.

Reduction of the ketone leads to the formation of *p*-propenyl-*o*-tolyl methyl ether, *p*-propyl-*o*-tolyl methyl ether, and 3-α-*hydroxypropyl-tolyl 6-methyl ether*, which is a viscid, colourless oil, boils at 157° under 2) mm., or at 160° under 22 mm. pressure, and has a sp. gr. 1·0419 at 15°/4°. The *phenylurethane* crystallises in slender needles and melts

at 78°. The *chloride*, when heated with pyridine at 110°, yields 3-*propenyl-o-tolyl methyl ether*, $OMe \cdot C_6H_3Me \cdot CH:CHMe$, which is a colourless oil, boils at 121—123° under 14 mm. pressure, has a sp. gr. 0·9844 at 16°/4° and n_D 1·5570 at 17°, and is oxidised by potassium permanganate to *o*-bromoanisic acid. The *nitrosochloride* forms small crystals and melts at 117°.

3-*Propyltolyl 6-methyl ether* is an oil, has an odour resembling that of phenol, boils at 222°, and has a sp. gr. 0·9361 at 18°/4° and n_D 1·5111.

2-*Propionyltolyl 5-methyl ether* melts at 43° and boils at 149—150° under 14 mm. pressure; the *oxime* melts at 94—95°. Reduction of the ketone leads to the formation of 2-propenyl-, 2-propyl-, and 2-α-hydroxypropyl-tolyl 5-methyl ethers.

2-α-*Hydroxypropyltolyl 5-methyl ether* is an odourless oil, has a burning, sweet flavour, boils at 149—151° under 13 mm. pressure, and has a sp. gr. 1·0478 at 18°/4°. The *phenylurethane* crystallises in colourless needles and melts at 94—95°. When heated with pyridine at 110°, the *chloride* yields 2-*propenyltolyl 5-methyl ether*, which boils at 119—121° under 13 mm. pressure and has a sp. gr. 0·9849 at 15°/4° and n_D 1·5555 at 15°. The *nitrosochloride*, $C_{11}H_{14}O_2NCl$, crystallises in small, colourless needles and melts at 108°. The 2-propenyltolyl 5-ether is oxidised by potassium permanganate in alkaline solution to *m*-homoanisic acid.

3-*Propionyltolyl 4-methyl ether* is a colourless oil, boils at 149—151° under 17 mm. pressure, has a sp. gr. 1·0523 at 14°/4°, forms an *oxime* which crystallises in colourless leaflets and melts at 92°, and is reduced by sodium and alcohol to the corresponding carbinol and small amounts of 3-propenyl- and 3-propyl-tolyl 4-methyl ethers. 3-α-*Hydroxypropyltolyl-4-methyl ether* is a colourless, odourless oil and boils at 153—154° under 22 mm. pressure; the *phenylurethane* crystallises in colourless leaflets and melts at 91°. When heated with pyridine at 120°, the *chloride* yields 3-*propenyltolyl 4-methyl ether*, which boils at 122—124° under 17 mm. pressure, can be titrated with bromine in carbon disulphide solution, does not yield a *nitrosochloride*, and is oxidised by alkaline potassium permanganate to 4-methoxy*iso*phthalic acid. 3-*Propyltolyl 4-methyl ether* is a colourless oil, has an odour resembling that of fusel oil, and boils at 216—218°.

p-ψ-Propenylanisole (Béhal and Tiffeneau, Abstr., 1901, i, 272) has a sp. gr. 0·9909 at 40°/0° and is reduced by sodium and alcohol to *p*-*iso*propylanisole, which boils at 95—96° under 19 mm., or at 212—213° under 756 mm. pressure, has a sp. gr. 0·94952 at 17°/4° and n_D 1·5045 at 17°, and is identical with Paternò and Spica's *p*-*iso*propylphenyl methyl ether (this Journal, 1877, i, 593).

2 : 5-*Dimethoxyacetophenone*, $C_6H_3Ac(OMe)_2$, obtained from acetic chloride and quinol dimethyl ether in presence of aluminium chloride, is a viscid oil, which boils at 156—158° under 15 mm. pressure and has a sp. gr. 1·1385 at 20°/4°. The *semicarbazone* crystallises in colourless needles and melts at 181—182°.

2 : 5-*Methoxy*-1-α-*hydroxy*iso*propylbenzene*, $C_6H_3(OMe)_2 \cdot CMe_2 \cdot OH$, is a colourless oil, which boils at 138—141° under 16 mm. pressure and has a sp. gr. 1·0854 at 25°/4°. When heated with pyridine at 125°,

the *chloride* yields 2 : 5-*methoxy*-1-*a*-*methylvinylbenzene*,

$C_6H_3(OMe)_2 \cdot CMe \colon CH_2$,

which is a mobile oil, boils at 124—125° under 15 mm. pressure, and has a sp. gr. 1·0382 at 22°/4° and n_D 1·536. iso*Propylquinol dimethyl ether* is a clear oil, boils at 114—116° under 15 mm. pressure, and has a sp. gr. 1·0129 at 17°/4° and n_D 1·5105 at 17°.

a-*Methyl*-p-*propenylanisole*, obtained by the action of magnesium ethyl iodide on acetylanisole, boils at 122—123° under 16 mm., or at 233—236° under 760 mm. pressure, has a sp. gr. 0·9827 at 20°/4° and n_D 1·5466. The *dibromide* formed by the action of bromine on methyl propenylanisole in carbon disulphide solution is an oil. p-*a*-*Methylpropylanisole*, $OMe \cdot C_6H_4 \cdot CHMeEt$, boils at 106—108° under 16 mm. pressure, has a sp. gr. 0·94336 at 20°/4° and n_D 1·5062.

p-*a*-*Ethylpropenylanisole*, $OMe \cdot C_6H_4 \cdot CEt \colon CHMe$, is formed by the action of magnesium ethyl iodide on ethyl anisate; it is a colourless oil, which boils at 129—130° under 17 mm. pressure, has a sp. gr. 0·9684 at 21°/4° and n_D 1·5062 at 20°, and is reduced by sodium and alcohol only with difficulty, as after three reductions the product had a sp. gr. 0·96155 and n_D 1·5273 at 22°. The action of magnesium propyl iodide on anisaldehyde leads to the formation of *p*-butenylanisole (Perkin, this Journal, 1877, ii, 671), which boils at 135—136° under 26 mm. pressure, has a sp. gr. 0·98648 at 15°/4° and n_D 1·5545 at 15°, and is reduced by sodium and alcohol to p-*butylanisole*,

$OMe \cdot C_6H_4 \cdot CH_2 \cdot CH_2Et$,

which boils at 120° under 19 mm. pressure, has a sp. gr. 0·9372 at 15°/4° and n_D 1·5027 at 15°, and forms a *sulphonic acid* crystallising in glistening leaflets.

m-*Butylolanisole*, formed by the action of magnesium propyl iodide on *m*-methoxybenzaldehyde, is a viscid, odourless oil, boils at 151—152° under 15 mm. pressure, and has a sp. gr. 1·0403 at 25°/4°; the *phenylurethane* melts at 63—64°. When heated with pyridine at 125°, the *chloride* yields m-*butenylanisole*, $OMe \cdot C_6H_4, CH \colon CHEt$, which is a mobile oil, boils at 128—129° under 16 mm. pressure, has a sp. gr. 0·987 at 25°/4° and n_D 1·5458 at 25°, decolorises potassium permanganate, and forms an *additive* compound with bromine. m-*Butylanisole* is a mobile oil, has a pleasant odour, boils at 115—116° under 19 mm. pressure, and has a sp. gr. 0·9393 at 22°/4° and n_D 1·5035 at 22°.

o-*Butenylphenetole*, $OEt \cdot C_6H_4 \cdot CH \colon CHEt$, formed by the action of magnesium propyl iodide on salicylaldehyde ethyl ether, is a colourless oil, boils at 126—127° under 19 mm. pressure, has a sp. gr. 0·97136 at 15°/4° and n_D 1·538 at 15°, decolorises potassium permanganate, forms an *additive* compound with bromine, and dissolves in concentrated sulphuric acid to a reddish-brown solution which, on addition of ice, forms a white, amorphous, flocculent precipitate. o-*Butylphenetole* is a mobile, highly refractive oil, boils at 124—125° under 19 mm. pressure, has a sp. gr. 0·9226 at 15°/4° and n_D 1·496 at 15°, and forms a crystalline *sulphonic acid*.

p-iso*Butenylphenetole*, obtained by reducing *iso*butyrylphenetole (Gattermann, Abstr., 1890, 964) with sodium and alcohol, boils at 128° under 15 mm. pressure, has a sp. gr. 0·9740 at 17°/4° and n_D 1·5472 at 17°, and can be titrated with bromine in carbon disulphide solution.

o-*Heptenylanisole*, $OMe \cdot C_6H_4 \cdot CH \colon CH \cdot C_5H_{11}$, formed by the action of

magnesium and *o*-iodoanisole on heptaldehyde, is a viscid oil, boils at 179° under 15 mm. pressure, and has a sp. gr. 0·99268 at 17°/4° and n_D 1·5087 at 17°. o-*Heptylanisole* is a mobile oil, boils at 153—155° under 20 mm. pressure, has a sp. gr. 0·91854 at 17°/4° and n_D 1·4956, and forms a *sulphonic acid* which crystallises in needles. G. Y.

Action of Bromine and Chlorine on Phenols: Substitution Products, ψ-Bromides and ψ-Chlorides. XI. Action of Bromine on 4-Hydroxydiphenylmethane. THEODOR ZINCKE and WILHELM WALTER (*Annalen*, 1904, **334**, 367—385. Compare this vol., i, 401). —4-Hydroxydiphenylmethane is readily prepared by the action of benzyl chloride on phenol in the presence of zinc; it forms silky needles and melts at 84°. Its *benzoyl* derivative forms needles and melts at 87°.

3 : 5-*Dibromo*-4-*hydroxydiphenylmethane*,

$$C_6H_5\cdot CH_2\cdot C{\lessgtr}{}^{CH:CBr}_{CH\cdot CBr}{\gtrless}C\cdot OH,$$

prepared by the gradual addition of the calculated amount of bromine to a cold solution of 4-hydroxydiphenylmethane in chloroform, exists in two crystalline modifications; one forms colourless needles and melts at 44°, the other forms rhombic crystals and melts at 57°. The former variety is unstable and passes readily into the latter on being left at the ordinary temperature. The *acetyl* derivative forms monoclinic prisms and melts at 53°.

3 : 5 : 4′-*Tribromo*-4-*hydroxydiphenylmethane*,

$$C_6H_4Br\cdot CH_2\cdot C{\lessgtr}{}^{CH:CBr}_{CH\cdot CBr}{\gtrless}C\cdot OH,$$

was prepared by agitating 4-hydroxydiphenylmethane with an excess of bromine until all had dissolved, and then crystallising the product obtained after removal of the bromine from petroleum, when slender needles, melting at 88°, separated. When its solution in glacial acetic acid is treated with sodium nitrite, one atom of bromine is replaced by one nitro-group. Its *acetyl* derivative melts at 105°.

2 : 3 : 5 : 6 : 4′-*Pentabromo*-4-*hydroxydiphenylmethane*, probably

$$C_6H_4Br\cdot CH_2\cdot C{\lessgtr}{}^{CBr:CBr}_{CBr\cdot CBr}{\gtrless}C\cdot OH,$$

prepared by allowing either 4-hydroxydiphenylmethane, its dibromo- or tribromo-derivative, to remain for a considerable time in presence of excess of bromine, separates from glacial acetic acid in silky needles and melts at 146—147°. The main product of the action consists, however, of ψ-bromides, the presence of which was recognised by their being precipitated as a yellow mass by the addition of water to the glacial acetic acid solution used in washing the pentabromo-compound just described.

Benzylidene-2 : 6-*dibromoquinone*, $C_6H_5\cdot CH:C{<}{}^{CH:CBr}_{CH:CBr}{>}CO,H_2O$,

prepared by the addition of the calculated quantity of bromine to a solution of dibromo-4-hydroxydiphenylmethane in carbon tetrachloride and then heating the mixture for four hours at 100°, forms a yellow, crystalline powder, which softens at 135—136°. The ψ-bromide was not obtained, and neither a ψ-bromide nor chloride could be prepared from the quinone itself. The latter is very readily transformed into *dibromo*-4-

hydroxydiphenylcarbinol, $C_6H_5\cdot CH(OH)\cdot C{<}^{CH:CBr}_{CH\cdot CBr}{>}C\cdot OH$, on simple exposure or by the action of alkali; it is also formed when the quinone in acetone solution is acted on by stannous chloride or bromide or when the quinone is boiled with glacial acetic acid and sodium acetate or with methyl alcohol; it crystallises in white needles which melt to a yellow solution at 164—165°. Its solution in sodium carbonate or in alkalis is colourless, whilst with sulphuric acid its solution is red, an indication that the quinone is regenerated.

Its *quinone* form, $C_6H_5\cdot CH(OH)\cdot CH{<}^{CH:CBr}_{CH:CBr}{>}CO$, formed from the hydrated benzylidenedibromoquinone by means of hydrochloric acid, forms leaflets and softens at 137—138°.

3 : 5-*Dibromo-4-hydroxydiphenylmethoxymethane*,

$$C_6H_5\cdot CH(OMe)\cdot C{<}^{CH:CBr}_{CH\cdot CBr}{>}C\cdot OH,$$

prepared by the action of methyl alcohol and sulphuric acid on the preceding compound or on the carbinol, separates from petroleum in white rhombohedra and melts at 126°. Its *acetyl* derivative separates from glacial acetic acid in needles and melts at 97°.

3 : 5-*Dibromo-4-hydroxydiphenylacetoxymethane*,

$$C_6H_5\cdot CH(OAc)\cdot CH{<}^{CH:CBr}_{CH:CBr}{>}CO$$

or $C_6H_5\cdot CH(OAc)\cdot C{<}^{CH:CBr}_{CH\cdot CBr}{>}C\cdot OH$, prepared either from the quinone or from the quinonoidal form of the carbinol, separates from dilute acetic acid in glistening needles and melts at 115° to a yellow solution.

The *acetyl* derivative, $C_6H_5\cdot CH(OAc)\cdot C{<}^{CH:CBr}_{CH\cdot CBr}{>}C\cdot OAc$, separates from dilute acetic acid in needles and from benzene in glistening, monoclinic prisms; it melts at 109°.

Benzylidenedibromoquinone was reduced by hydriodic acid to dibromo-4-hydroxydiphenylmethane. A. McK.

Two Modifications of α-Nitrosoresorcinol Monoethyl Ether. FERDINAND HENRICH (*J. pr. Chem.*, 1904, [ii], 70, 313—325. Compare Kietaibl, Abstr., 1899, i, 343; 1900, i, 163; 1902, i, 447; 1903, i, 88).—α-Nitrosoresorcinol monoethyl ether separates from alcohol in yellow, rhombic crystals, melts at 147—148°, and, when recrystallised from benzene, toluene, xylene, or carbon disulphide, is converted into the labile *modification*, which separates in green, dichroic crystals and sinters at 127°, changes into the yellow modification at 128—130°, or at 130—140° if rapidly heated, and, on further heating, melts at 147—148°. If formed from the crude ether, it immediately commences to change again into the yellow ether, the change being complete in about a day, but if obtained from the purified ether the reverse change takes place more slowly and may require some weeks for completion.

The action of ethyl iodide on the potassium derivative of α-nitrosoresorcinol monoethyl ether leads to the formation of the *diethyl* ether, $OEt\cdot C_6H_3O:N\cdot OEt$, which forms orange-coloured, crystalline aggregates

and melts at 89·5—91·5°. When reduced with stannous chloride and hydrochloric acid, it yields the hydrochloride of 5-ethoxy-2-aminophenol.

The action of phenylcarbimide on *a*-nitrosoresorcinol monoethyl ether dissolved in benzene, alcohol, or other solvent at the laboratory temperature leads to the immediate formation of the *urethane*,

$$NHPh{\cdot}CO{\cdot}O{\cdot}N{:}C_6H_3O{\cdot}OEt,$$

which crystallises in leaflets and, when boiled with alcohol, yields the yellow nitroso-compound. If the reaction is carried out at 6°, it takes place immediately in the alcoholic, but only after 15 minutes in the benzene, solution.

The yellow, stable modification of *a*-nitrosoresorcinol monoethyl ether is considered to be an *o*-quinoneoxime,

$$OEt{\cdot}C{<}\begin{matrix}CH{\cdot}CO\\CH{:}CH\end{matrix}{>}C{:}N{\cdot}OH,$$

and the green, labile modification an *o*-nitrosophenol,

$$OEt{\cdot}C{<}\begin{matrix}CH{\cdot}C(OH)\\CH{=\!=}CH\end{matrix}{>}C{\cdot}NO.$$

G. Y.

Action of Nitrous Acid on Resorcinol Monomethyl Ether. FERDINAND HENRICH and HEINRICH EISENACH (*J. pr. Chem.*, 1904, [ii], **70**, 332—341. Compare Abstr., 1902, i, 447).—The soluble, brown nitrosoresorcinol monomethyl ether, previously described as melting at 138°, is now found to be impure, labile 2-nitroso-5-methoxyphenol.

The yellow, stable 2-nitroso-5-methoxyphenol forms prismatic crystals; the green, labile nitroso-ether forms dichroic crystals, becomes yellow at 130—140° when rapidly heated, melts at 158—159°, and is slightly more stable than the corresponding ethyl ether. Phenylcarbimide reacts with 2-nitroso-5-methoxyphenol at 7°, immediately in alcoholic, slowly in benzene, solution, to form the *urethane*, $NHPh{\cdot}CO{\cdot}ON{:}C_6H_3O{\cdot}OMe$, which sinters at 162° and melts at 168°.

Both the yellow and the green modifications of the methyl ether form the same *sodium* derivative, which, in aqueous solution, has a neutral reaction and yields the yellow ether on acidification. When treated with methyl iodide, the silver derivative yields the dimethyl ether, $OMe{\cdot}C_6H_3O{:}N{\cdot}OMe$, which crystallises in yellow prisms, melts at 115—117°, dissolves in organic solvents to yellow solutions, and, when reduced by stannous chloride and hydrochloric acid, yields 2-amino-5-methoxyphenol.

The constitutional formula $OMe{\cdot}C{<}\begin{matrix}CH{\cdot}CO\\CH{:}CH\end{matrix}{>}C{:}N{\cdot}OH$ is ascribed to the yellow, $OMe{\cdot}C{<}\begin{matrix}CH{\cdot}C(OH)\\CH{=\!=}CH\end{matrix}{>}C{\cdot}NO$ to the green, modification.

G. Y.

Action of Nitric Acid on Phloroglucinyl Methyl Ether. [HERMANN THOMS and] CARL MANNICH (*Arch. Pharm.*, 1904, **242**, 501—512. Compare Will, Abstr., 1888, 457).—The ether can be obtained in good yield by boiling phloroglucinol with methyl alcohol

and concentrated sulphuric acid, isolating the crude product, and methylating it further with 40 per cent. aqueous potassium hydroxide and methyl sulphate. When shaken for an hour or two with 10 per cent. nitric acid at 50—60°, it is converted into dimethoxybenzoquinone. When it is stirred with warm 33 per cent. nitric acid, a blue colouring matter soon separates. This is reduced by sulphurous acid to a colourless substance melting at 142°, which has very feeble basic properties, forms a *nitrosoamine* melting at 193°, and yields the dimethoxyquinone on oxidation; the percentages of C, H, N, and OMe correspond with *hexamethoxydiphenylamine*, $C_{18}H_{23}O_6N$, or

$$NH\left[C{<}\begin{matrix}C(OMe){:}CH\\C(OMe){\cdot}CH\end{matrix}{>}C{\cdot}OMe\right]_2.$$

Presumably this is the leuco-base corresponding with the colouring-matter, which may have the formula

$$CH_2{\cdot}O{\cdot}C{<}\begin{matrix}CH{:}C(OMe)\\CH{\cdot}C(OMe)\end{matrix}{>}C{\cdot}N{\cdot}C{<}\begin{matrix}C(OMe){:}CH\\C(OMe){\cdot}CH\end{matrix}{>}C{\cdot}OMe.$$

The colouring-matter is the *nitrate* of the latter base; when treated with alcoholic potassium hydroxide, it yields the *base* itself,

$$C_{18}H_{21}O_6N,EtOH,$$

as red needles containing alcohol of crystallisation; only 5 methoxyl groups are now present. When left for 2 days in contact with a solution of potassium hydroxide in dilute alcohol, it is converted into a colourless substance, $C_{17}H_{21}O_5N$, melting at 131—133°, which forms a nitrosoamine and generally resembles the leuco-base in appearance and in properties; presumably it is *pentamethoxydiphenylamine*.

C. F. B.

2:3-Dihydroxynaphthalene. THEODOR ZINCKE and K. FRIES (*Annalen*, 1904, 334, 342—366).—By the action of an excess of chlorine on a solution of 2 : 3-dihydroxynaphthalene in glacial acetic acid, *tetrachloro*-2 : 3-*diketotetrahydronaphthalene*, $C_6H_4{<}\begin{matrix}CCl_2{\cdot}CO\\CCl_2{\cdot}CO\end{matrix}$, is formed as a white, crystalline powder, which crystallises from a mixture of benzene and petroleum in needles and melts at 115°. It contains $1\frac{1}{2}H_2O$. When reduced by stannous chloride, it forms dichlorodihydroxynaphthalene; when added to nitric acid of sp. gr. 1·5, which is cooled, it dissolves without undergoing oxidation, and, when water is carefully added, the *additive compound*, $C_{10}H_4Cl_4O_2,HNO_3$, separates in the form of needles, which melt and decompose at 152°. Phthalic acid is produced when tetrachloro-2 : 3-diketotetrahydronaphthalene is boiled with concentrated nitric acid.

1 : 4-*Dichloro*-2 : 3-*dihydroxynaphthalene*, $C_6H_4{<}\begin{matrix}CCl{:}C{\cdot}OH\\CCl{:}C{\cdot}OH\end{matrix}$, prepared as already indicated or by the chlorination of 2 : 3-dihydroxynaphthalene, crystallises in colourless prisms and melts at 181°. Its *acetyl* derivative forms small plates and melts at 140·5°. The quinone corresponding with 1 : 4-dichloro-2 : 3-dihydroxynaphthalene could not be prepared. When oxidised by boiling with concentrated nitric acid, phthalic acid was formed. It dissolves without decomposition in sodium carbonate and in dilute alkalis. When mixed at the ordinary tem-

perature with five times its weight of nitric acid (sp. gr. 1·4), it dissolves, and then *dichlorodinitro-2 : 3-diketotetrahydronaphthalene*,

$$C_6H_4<\begin{matrix}CCl(NO_2)\cdot C(OH)_2\\ |\\ CCl(NO_2)\cdot C(OH)_2\end{matrix} \text{ or } C_6H_4<\begin{matrix}CCl(NO_2)\cdot CO\\ |\\ CCl(NO_2)\cdot CO\end{matrix},2H_2O,$$

separates; this forms colourless plates, melts and decomposes at 155°, forms phthalic acid when its solution in alkalis is heated, and dissolves in concentrated sulphuric acid with evolution of gas to form a deep blue solution.

Tetrachloroketohydrinden, $C_6H_4<\begin{matrix}CCl_2\\ CCl_2\end{matrix}>CO$, formed by the action of bleaching powder on a solution of tetrachloro-2 : 3-diketotetrahydronaphthalene in glacial acetic acid, forms triclinic pyramids and melts at 98°. Its formation is accounted for by supposing that water is added on to the keto-chloride, when one of the rings is disrupted with the probable formation of the intermediate compound,

$$C_6H_4(CCl_2H)\cdot CCl_2\cdot CO\cdot CO_2H,$$

which then forms hydroxyhydrindenecarboxylic acid,

$$C_6H_4<\begin{matrix}CCl_2\\ CCl_2\end{matrix}>C(OH)\cdot CO_2H,$$

from which carbon dioxide and water are eliminated during its oxidation. Tetrachloroketohydrinden is readily converted by alkali hydroxide into phthalidecarboxylic acid, $C_6H_4<\begin{matrix}CO\\ CH(CO_2H)\end{matrix}>O$, crystallising in leaflets or needles melting at 153°, and yielding phthalide when heated at about 215°. During its formation, an aldehydic ketonic acid, $CHO\cdot C_6H_4\cdot CO\cdot CO_2H$, is probably produced as an intermediate product which, by the addition of water, forms a lactonic acid, $CO_2H\cdot C_6H_4\cdot CH(OH)\cdot CO_2H$, which then loses water, being converted into its lactone, phthalidecarboxylic acid.

Phthalonic acid is formed when tetrachloroketohydrindene is acted on by nitric acid of sp. gr. 1·5 at the ordinary temperature.

Dichloro-2 : 3-naphthaphenazine, $C_{16}H_8N_2Cl_2$, prepared by the action of *o*-phenylenediamine on tetrachloro-2 : 3-diketotetrahydronaphthalene in glacial acetic acid solution, separates from chloroform in glistening needles and melts at 265°. Its solution in concentrated sulphuric acid is dark brown; when water is added, an intensely green coloration appears.

It was not found possible to oxidise 2 : 3-dihydroxynaphthalene to the corresponding quinone.

1 : 4-*Dibromo-2 : 3-dihydroxynaphthalene*, prepared by the addition of bromine (2 parts) to a solution of 2 : 3-dihydroxynaphthalene (1 part) in glacial acetic acid (5 parts), separates from chloroform in colourless needles and melts at 178°. 2 : 3-Dihydroxynaphthalene is regenerated from it by the action of stannous chloride. When heated with concentrated nitric acid of sp. gr. 1·4, it forms phthalic acid. Its *acetyl* derivative forms glistening leaflets and melts at 175°.

1 : 4 : 6 : 7-*Tetrabromo-2 : 3-dihydroxynaphthalene*, prepared by the addition of bromine (5 parts) to a solution of 2 : 3-dihydroxynaphthalene (1 part) in glacial acetic acid (10 parts), crystallises from chloroform in colourless needles and melts at 242°. It forms 6 : 7-dibromo-2 : 3-dihydroxynaphthalene when reduced by stannous chloride.

When oxidised by nitric acid of sp. gr. 1·4, it forms 4 : 5-dibromophthalic acid. Its *acetyl* derivative crystallises in needles and melts at 237°.

When a concentrated solution of stannous chloride is gradually added to a boiling solution of 1 : 4 : 6 : 7-tetrabromo-2 : 3-dihydroxynaphthalene (1 part) in glacial acetic acid (20 parts) and the product then acidified by hydrochloric acid, 6 : 7-*dibromo*-2 : 3-*dihydroxynaphthalene* is formed. It separates from benzene in silvery leaflets and from dilute alcohol in needles, melts at 217°, and is converted by warming with nitric acid of sp. gr. 1·4 into 4 : 5-dibromophthalic acid. Its *acetyl* derivative forms needles and melts at 155°.

Dibromodinitro-2 : 3-*diketotetrahydronaphthalene*,

$$C_6H_4<\begin{matrix}CBr(NO_2)\cdot C(OH)_2\\ | \\ CBr(NO_2)\cdot C(OH)_2\end{matrix} \text{ or } C_6H_4<\begin{matrix}CBr(NO_2)\cdot CO\\ | \\ CBr(NO_2)\cdot CO\end{matrix},2H_2O,$$

prepared by the addition of 1 : 4-dibromo-2 : 3-hydroxynaphthalene (1 part) to nitric acid of sp. gr. 1·51—1·52 (3 parts), separates from benzene in prisms and melts and decomposes at 134°. A. McK.

Cholesterol. III. ADOLF WINDAUS and G. STEIN (*Ber.*, 1904, 37, 3699—3708. Compare this vol., i, 49).—Assuming the formula $C_{27}H_{44}O$ for cholesterol, the authors are of opinion that the molecule consists of a complex of 5 reduced benzene rings; one of these (β) contains a double linking, and another (α) a secondary hydroxyl group. It is probably derived from a 5-ring hydrocarbon related to reduced retene. If the formula for cholesterol is written

$$\begin{matrix}OH\cdot \overset{\alpha}{C}H-\\ | \\ CH_2\end{matrix}>C_{23}H_{38}<\begin{matrix}\overset{\beta}{C}H\\ \| \\ CH\end{matrix},$$

then its transformation into the tetracarboxylic acid,

$$(CO_2H)_2C_{23}H_{38}(CO_2H)_2,$$

by the following process is explained.

Phosphorus pentachloride reacts with a chloroform suspension of cholestanonol yielding *β-chlorocholestanone*, $\begin{matrix}CHCl\\ | \\ CH_2\end{matrix}>C_{23}H_{38}<\begin{matrix}CO\\ | \\ CH_2\end{matrix}$, which crystallises from acetic acid in colourless needles melting at 180—181°; it yields an *oxime* melting at 179—181°, and a mono*bromo*-derivative melting at 116—117°. The chlorinated ketone is isomeric with Mauthner and Suida's α-compound melting at 128·5—129° (this vol., i, 50), and is very stable towards all oxidising agents, with the exception of nitric acid, which converts it into the *dibasic acid*, $\begin{matrix}CHCl\\ | \\ CH_2\end{matrix}>C_{23}H_{38}(CO_2H)_2$; this crystallises from acetic acid in needles melting at 243° and is very sparingly soluble in all solvents. Its *ethyl* ester melts at 142—143° and the *anhydride* at 187°. When warmed with 10 per cent. aqueous potash, the chloro-acid yields the corresponding *dibasic hydroxy-acid*, $C_{27}H_{44}O_5$, which crystallises from acetone and water in large plates melting, when quickly heated, at 239—240°. It appears to contain $1HO_2$, gives crystalline *magnesium*, *barium*, and *ethyl* salts, and with acetyl chloride

yields the *anhydride*, $C_{27}H_{42}O_4$, which sinters at 210° and melts to a clear liquid at 214°.

The hydroxy-acid, on oxidation with an acetic acid solution of chromic anhydride, yields the *ketonic acid*, $\begin{matrix}\overset{\alpha}{CO}- \\ | \\ CH_2\end{matrix}\!\!>C_{23}H_{38}(CO_2H)_2$, which is isomeric with the ketonic dibasic acid previously described (this vol., i, 49) and now represented as $(CO_2H)_2C_{23}H_{38}<\begin{matrix}\overset{\beta}{CO} \\ | \\ CH_2\end{matrix}$, as the carboxylic groups in the two compounds are obtained by the oxidation of different rings of the cholesterol molecule. The new acid crystallises in long, compact needles, melts at about 255°, and is readily soluble in acetone or methyl or ethyl alcohol; the *oxime* melts at 213—214°. On oxidation with chromic anhydride, the ketonic acid yields the *tetracarboxylic acid*, $C_{23}H_{38}(CO_2H)_4$, which crystallises from a mixture of ether and benzene in needles, and melts and decomposes at about 174°. It dissolves readily in alcohol, but only sparingly in benzene.
J. J. S.

Products similar to Cholesterol in Bresk from Borneo. J. SACK and BERNHARD TOLLENS (*Ber.*, 1904, **37**, 4110—4114).—On subjecting bresk, the product obtained on coagulating the sap of *Alstonia costulata* (*Dryera costulata*), to fractional extraction with alcohol, three crystalline products have been obtained. Using alcohol of 70° Tr. for extraction, a substance *alstol*, $C_{24}H_{38}O$, crystallising in colourless needles melting at 158° is obtained, and having $[\alpha]_D$ +56·4°. *Alstol dibromide* crystallises in yellow platelets melting at 135—138°, whilst the *benzoate*, which also crystallises in flat plates, melts at 254° and the *acetate* at 200°. Alstol gives most of the colour reactions of the cholesterol group, but is not identical with *iso*cholesterol. When the bresk residues are extracted with alcohol of 95° Tr., two other products are obtained. *Alstonin*, $C_{14}H_{22}O$, melts at 191—192° and has $[\alpha]_D$ +49°. iso*Alstonin*, $C_{14}H_{22}O$, crystallises in platelets melting at 163°, having $[\alpha]_D$ +65·5°. The bresk residues dissolved in carbon disulphide and purified by precipitation of the impurity with alcohol give, on evaporation, a white, elastic mass, $C_{21}H_{32}O$, melting at 125°.
E. F. A.

Lupeol from the Bark of Roucheria Griffithiana. J. SACK and BERNHARD TOLLENS (*Ber.*, 1904, **37**, 4105—4109).—The bark of *Roucheria Griffithiana*, when extracted with 85 per cent. alcohol, yields a crystalline product identical with the lupeol obtained by Likiernik (Abstr., 1891, 551) from the husks of *Lupinus luteus*. The product from *Roucheria* melts at 213° (corr.), has the composition $C_{26}H_{42}O$, a molecular weight, determined ebullioscopically, of 430, and $[\alpha]_D$ +27·4°; the benzoate crystallises in prisms melting at 262°, the *dibromide* forms colourless platelets melting at 154°. The acetate described by Likiernik could not be obtained. On heating with phenylcarbimide, a compound melting at 226° was formed, having the

composition $C_{26}H_{41}ON$ or $C_{27}H_{41}ON$. After the separation of the lupeol, the mother liquors were proved to contain dextrose.

E. F. A.

Electrolytic Reduction of Aromatic Esters. CARL METTLER (*Ber.*, 1904, 37, 3692—3696. Compare Tafel, this vol., i, 849).—When methyl benzoate, dissolved in a mixture of concentrated sulphuric acid, water, and alcohol, is reduced in a divided cell by means of lead electrodes for 6 hours at 15—25° with a current of 15 amperes, the chief products are benzyl alcohol and benzyl methyl ether, $C_6H_5{\cdot}CO_2Me + 4H = C_6H_5{\cdot}CH_2{\cdot}OH + MeOH$ or

$$= C_6H_5{\cdot}CH_2{\cdot}OMe + H_2O.$$

Probably a compound $C_6H_5{\cdot}CH(OH){\cdot}OMe$ is first formed. The benzyl alcohol is removed as benzyl hydrogen phthalate by means of phthalic anhydride.

Ethyl benzoate, ethyl *m*-bromobenzoate, and ethyl *o*-chlorobenzoate behave in a similar manner, but the yield of alcohol is much smaller with the halogen compounds. *Benzyl methyl ether* boils at 168°, *benzyl ethyl ether* at 185°, m-*bromobenzyl ethyl ether* at 237°, o-*chlorobenzyl ethyl ether* at 212°, and o-*chlorobenzyl alcohol* crystallises in colourless needles melting at 72°.

J. J. S.

Unsaturated Compounds. F. WILLY HINRICHSEN (*Annalen*, 1904, 336, 168—227).—The first part of this paper is an elaboration of the author's views published previously (Abstr., 1902, i, 129).

Contrary to Thiele's theory, the formation of additive compounds from a compound containing conjugated ethylene linkings does not result necessarily in addition at the ends of the conjugated system, but is influenced by the electro-chemical characters of the atoms taking part in the reaction, by the relation to each other of the atoms or atomic groupings added, and by substituting groups already present in the unsaturated compound.

[With WILHELM TRIEPEL.]—*Methyl cinnamylideneacetate*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2Me,$$

obtained by boiling the acid with methyl alcohol and hydrochloric acid, crystallises in glistening, white scales and melts at 71°.

With hydrogen bromide in ethereal solution, methyl cinnamylidenemalonate forms an *additive* compound, $CHPh{:}CH{\cdot}CHBr{\cdot}CH(CO_2Me)_2$, which loses hydrogen bromide in a desiccator over potassium hydroxide, when heated or when treated with methyl-alcoholic potassium hydroxide; no product could be obtained on reduction, but on oxidation with chromic acid it yields benzoic acid. With sodium ethoxide in ethereal solution, methyl cinnamylidenemalonate forms a hygroscopic *additive* compound, $CHPh{:}CH{\cdot}CH(OEt){\cdot}CHNa(CO_2Me)_2$, which on hydrolysis yields the original ester and is oxidised by chromic acid to benzoic acid.

The action of ammonia on cinnamylideneacetic acid leads to the formation of the *ammonium* salt which melts at 173° (compare Perkin, Trans., 1877, 31, 403). The acid chloride is not formed by the action of phosphorus pentachloride or thionyl chloride on the acid.

[With Marie Reimer.]—*a-p-Nitrophenylcinnamenylacrylic acid,*

$$CHPh:CH\cdot CH:C(C_6H_4\cdot NO_2)\cdot CO_2H,$$

obtained from cinnamaldehyde and sodium *p*-nitrophenylacetic acid in presence of acetic anhydride, crystallises in yellow leaflets and melts and decomposes at 258—259°; the *sodium* salt contains $2H_2O$; the *methyl* ester crystallises in lemon-coloured needles and melts at 130—131°; the *nitrile*, obtained from cinnamaldehyde and *p*-nitrobenzyl cyanide in presence of sodium ethoxide, crystallises in small, orange-coloured needles and melts at 209—210°. The action of bromine on *a-p*-nitrophenylcinnamenylacrylic acid in carbon disulphide solution leads to the formation of the *dibromide,*

$$CHBrPh\cdot CHBr\cdot CH:C(C_6H_4\cdot NO_2)\cdot CO_2H,$$

which forms yellow crystals and melts at 207—209°. If the bromination is carried out in chloroform solution, a *bromo-δ-lactone* is formed in addition to the dibromide. The *methyl* ester, $C_{17}H_{12}O_4NBr_2Me$, melts at 133—135°; the *nitrile* forms yellow crystals and melts at 179—180°.

[With Wilhelm Triepel.]—The action of a limited amount of bromine on cinnamenylacrylic acid in chloroform solution leads to the formation of a yellow *substance* which melts at 115—120°, and may be a mixture of tetrabromide and unchanged acid. With more bromine, the *tetrabromide,* which crystallises in white needles and melts at 245°, is obtained.

The action of a limited quantity of bromine on the methyl ester in carbon disulphide solution leads to the formation of the *dibromide,* $CHPh:CH\cdot CHBr\cdot CHBr\cdot CO_2Me$, which melts at 126° and is oxidised by chromic acid to benzoic acid. The *tetrabromide* crystallises in white needles and melts at 150°.

The *dibromide* of methyl cinnamylidenemalonate forms white crystals and melts at 93°; it reduces silver oxide in alcoholic solution, and is oxidised by chromic acid to dibromocinnamic acid. The *tetrabromide* melts at 135°. The action of hydrogen bromide on the dibromide leads to the formation of a *tribromo*-compound.

The action of bromine on phenylcinnamenylacrylic acid in carbon disulphide solution leads to the formation of a substance which melts at 135° and is oxidised to benzoylformic acid (compare Thiele and Rössner, Abstr., 1899, i, 612). G. Y.

A New Method of Esterifying Organic Acids. Alfred Werner and W. Seybold (*Ber.*, 1904, **37**, 3658—3661).—By the action of methyl sulphate on aqueous solutions of the alkali salts of organic acids, it is possible to obtain the corresponding methyl esters. In this way it is also possible to prepare esters of acids such as 2 : 4 : 6-tribromobenzoic acid, which, owing to steric retardation, cannot be esterified by the ordinary methods. The method is applied to acetic, *iso*valeric, stearic, and tribromobenzoic acids; in the last case, a methyl ester melting at 68° was obtained, identical with that previously prepared in small quantities by Wegscheider. *Methyl* 2 : 4 : 6-*trinitrobenzoate* crystallises from alcohol in colourless platelets melting at 158°; *methyl β-methoxy-a-naphthoate* forms colourless crystals melting

at 52°; *methyl β-methoxy-β-naphthoate* crystallises in colourless needles melting at 49°. E. F. A.

Esterification of Carboxylic Acids by means of Methyl Sulphate. HANS MEYER (*Ber.*, 1904, 37, 4144—4145).—It is pointed out that the method of esterifying carboxylic acids with methyl sulphate, described as new by Werner and Seybold (preceding abstract), was used by Dumas and Peligot so far back as 1835, and subsequently by Wegscheider and by the author. E. F. A.

Application of Kolbe's Salicylic Acid Synthesis to Benzene Compounds containing Nitrogen. JOSEF HOUBEN (*Ber.*, 1904, 37, 3978—3981).—Magnesium methyl iodide was added to methylaniline and a current of dry carbon dioxide passed into the product, when the white precipitate of the magnesium compound of methylaniline dissolved. The ethereal solution was then heated at 140—200° for 20 hours. The phenylcarbamate initially formed is transformed under these conditions into p-*methylaminobenzoic acid*, which separates from methylated spirit in red needles and melts at 228—229°. A. McK.

Transformation of βγ-Unsaturated α-Hydroxy-acids into the Isomeric γ-Ketonic Acids. JOSEF HOUBEN (*Ber.*, 1904, 37, 3981—3983).—A criticism of the views of Erlenmeyer, jun. (this vol., i, 892), respecting the transformation of βγ-unsaturated α-hydroxy-acids into the isomeric γ-ketonic acids when αβ-unsaturated lactones are formed as intermediate products. A. McK.

Preparation of Anisoyl Peroxide. LUDWIG VANINO and E. UHLFELDER (*Ber.*, 1904, 37, 3624).—*Anisoyl peroxide*,

$$O_2(CO\cdot C_6H_4\cdot OMe)_2,$$

prepared by the oxidation of a solution of anisoyl chloride in acetone by a mixture of hydrogen peroxide and pyridine at 0°, melts at 128° and explodes on the addition of concentrated sulphuric acid.

A. McK.

Esterification of Organic Acids. HANS VON LIEBIG (*Ber.*, 1904, 37, 4036—4038. Compare Werner and Seybold, this vol., i, 1013).—The action of methyl sulphate on *m*-dihydroxytriphenylmethanecarboxylic lactone (Abstr., 1903, i, 828) in aqueous potassium hydroxide solution leads to the formation of methyl dimethoxytriphenylmethanecarboxylate, $C_6H_3(OMe)_2\cdot CPh_2\cdot CO_2Me$, which crystallises in glistening, rhombic leaflets and melts at 168°, dimethoxytriphenylmethanecarboxylic acid, which crystallises in four-sided prisms and melts at 246°, and hydroxymethoxytriphenylmethanecarboxylolactone, which forms rhombohedric crystals and melts at 181°. The dimethoxy-acid yields the methyl ester when treated with methyl sulphate; it is very stable towards hydrolysing agents, but is partially converted into the monomethoxy-lactone by treatment with boiling acetic chloride.

When treated with ethyl sulphate, dihydroxytriphenylmethanecarboxylolactone yields the ethoxy-lactone and the diethoxy-acid, but no ethyl ester. G. Y.

α-Ketonic Acids and their Transformations. Emil Erlenmeyer, jun. (*Annalen*, 1904, 333, 160—227. Compare Abstr., 1902, i, 543).—In this paper, a complete summary of the work carried out in recent years on the α-ketonic acids and the changes which they undergo is given. The mechanism of the reactions of the ketonic acids is discussed from a stereo-chemical standpoint. K. J. P. O.

α-Oxy-lactones and their Transformations. α-Oxy-β-phenyl-γ-benzyl-, α-Oxy-βγ-diphenyl-, and α-Oxy-β-nitrophenyl-γ-phenylbutyrolactone. Emil Erlenmeyer, jun., and E. Arbenz (*Annalen*, 1904, 333, 228—237).—To prepare the phenylpyruvic acid required in the preparation of the oxylactones, phenylcyanopyruvic acid was boiled with dilute sulphuric acid, α-oxy-β-phenyl-γ-benzylbutyrolactone being produced in considerable amount as a by-product. *α-Oxy-βγ-diphenylbutyrolactone* was obtained by condensing phenylpyruvic acid with benzaldehyde in the presence of hydrogen chloride. The *acetyl* derivative of the first mentioned oxylactone,

$$\begin{array}{l}\mathrm{CPhAc\cdot CH\cdot CH_2Ph} \\ \;| \qquad\quad\;\; | \\ \mathrm{CO{-}CO{-}O}\end{array},$$

crystallises in needles melting at 91°, whilst the *acetyl* derivative of the oxydiphenylbutyrolactone melts at 115°; both acetyl derivatives yield the original lactones on hydrolysis with hydrochloric acid.

When reduced with zinc and acetic acid, α-oxy-βγ-diphenylbutyrolactone is converted into desylacetic acid, diphenylcrotonolactone, and an *acid*, $\mathrm{CHPh{:}CPh\cdot CH(OH)\cdot CO_2H}$, which is decomposed on heating with 10 per cent. sodium hydroxide into dibenzyl and oxalic acid. When treated with bromine (1 mol.) in chloroform solution and the solvent carefully evaporated, two bromo-derivatives are obtained; the one is the *dibromide* of the acid, $\mathrm{CHBrPh\cdot CBrPh\cdot CH(OH)\cdot CO_2H}$, which crystallises in transparent, rhombic crystals, becoming brown at 140° and decomposing at 144°, and the other is a *bromo-lactone*,

$$\mathrm{CBrPh}{<}\begin{array}{l}\mathrm{CHPh{-}O} \\ \qquad\quad\;\; | \\ \mathrm{CH(OH)\cdot CO}\end{array},$$

which crystallises in needles resembling asbestos, melting and decomposing at 105°. When boiled with alcohol, both compounds are reconverted into the original oxybutyrolactone.

α-Oxy-β-nitrophenyl-γ-phenylbutyrolactone,

$$\mathrm{NO_2\cdot C_6H_4\cdot CH}{<}\begin{array}{l}\mathrm{CO{-}CO} \\ \qquad\;\;\; | \\ \mathrm{CHPh\cdot O}\end{array},$$

is prepared by condensing molecular proportions of benzaldehyde and nitrophenylpyruvic acid by the aid of hydrogen chloride and forms pale yellow, monoclinic crystals melting at 171°, which give a red coloration with alcoholic ferric chloride. The *benzoyl* derivative forms colourless rhombohedra melting at 162°, and the *acetyl* derivative slender needles melting at 118°. K. J. P. O.

Two Stereoisomeric α-Oxy-β-phenyl-γ-p-*iso*propylphenylbutyrolactones and their Transformations. Emil Erlenmeyer, jun., and C. Kehren (*Annalen*, 1904, 333, 238—254).—Cuminalde-

hyde and phenylpyruvic acid yield the *oxy-lactone*,

$$C_6H_4Pr^\beta\cdot CH<\begin{matrix}CHPh\cdot CO\\ | \\ O\text{———}CO\end{matrix},$$

which crystallises in monoclinic plates [$a:b:c=0.6693:1:0.9101$; $\beta=81°51'$] melting at 186°. The *acetyl* derivative crystallises in colourless plates melting at 120°, and the *benzoyl* derivative forms prismatic crystals melting at 140°. When the lactone is heated above its melting point, iso*propylstilbene*, $CHPh:CH\cdot C_6H_4Pr^\beta$, is obtained as colourless leaflets melting at 85°; the *dibromide* forms colourless leaflets, becoming brown at 172° and melting and decomposing at 181°.

When reduced with sodium amalgam, the oxy-lactone is converted into *α-hydroxy-β-phenyl-γ-*iso*propylphenylbutyrolactone*,

$$C_6H_4Pr^\beta\cdot CH<\begin{matrix}CHPh\cdot CH\cdot OH\\ | \\ O\text{———}CO\end{matrix},$$

which crystallises in rhombic needles melting at 169°, and when boiled with barium hydroxide yields the αγ-dihydroxy-acid. On reduction with zinc dust and acetic acid, a *γ-ketonic acid*,

$$C_6H_4Pr^\beta\cdot CO\cdot CHPh\cdot CH_2\cdot CO_2H,$$

crystallising in prisms melting at 111°, an unsaturated *acid*, $C_6H_4Pr^\beta\cdot CH:CPh\cdot CH(OH)\cdot CO_2H$, which crystallises in colourless needles melting at 136°, and an unsaturated lactone are produced. The bromine additive product of the unsaturated acid yields, when boiled with alcohol, the original α oxy-lactone and its stereoisomeride melting at 198°. The unsaturated *lactone*, which crystallises in silky needles melting at 124° and is converted into the γ-ketonic acid (m. p. 111°) by boiling with dilute acids or alkalis, is probably represented by the formula $C_6H_4Pr^\beta\cdot C<\begin{matrix}CPh\cdot CH_2\\ | \\ O\text{—}CO\end{matrix}$, since it yields, when condensed with benzaldehyde in the presence of aniline or piperidine, the product $C_6H_4Pr^\beta\cdot C<\begin{matrix}CPh\cdot C:CHPh\\ | \\ O\text{—}CO\end{matrix}$, which crystallises in yellow needles melting at 143°. The unsaturated acid is converted into the lactone and the γ-ketonic acid by boiling with 12 per cent. hydrochloric acid, and quantitatively into the lactone by treatment with acetic anhydride in the presence of sulphuric acid.

The isomeric *α-oxy-β-phenyl-γ-*p-iso*propylbutyrolactone* was mainly obtained when the condensation took place at a lower temperature during the winter months, and crystallised in centric groups of needles easily distinguishable from the plates of the isomeride, melting at 198°; the *acetyl* derivative forms needles melting at 158°, and the *benzoyl* derivative needles melting at 126°. K. J. P. O.

Condensation of Phenylpyruvic Acid with Piperonaldehyde, Cinnamaldehyde, and Furfuraldehyde. EMIL ERLENMEYER, jun., and A. BRAUN (*Annalen*, 1904, **333**, 254—268).—When phenylpyruvic acid is condensed with piperonaldehyde in acetic acid solution by means of hydrogen chloride, two isomeric *lactones* are produced, $CH_2:O_2:C_6H_3\cdot CH<\begin{matrix}CHPh\cdot CO\\ | \\ O\text{———}CO\end{matrix}$, which differ in their solubility in

alcohol and in crystalline habit; the more soluble melts at 208° and yields an *acetyl* derivative which crystallises in needles melting at 135°, and a *benzoyl* derivative melting at 179°; the less soluble melts at 205°, its *benzoyl* derivative at 172°, and its *acetyl* derivative, which crystallises in leaflets, at 130°. The latter lactone is reduced by 4 per cent. sodium amalgam to the corresponding *a-hydroxy-lactone*, which crystallises in needles melting at 153°, and forms an *acetyl* derivative crystallising in leaflets melting at 116—117°. On reducing the lactone, melting at 208°, with sodium amalgam, a *hydroxy-lactone*, which crystallises in needles melting at 155°, is produced; its optical behaviour distinguishes it from the hydroxy-lactone (m. p. 153°) just mentioned.

When the hydroxylactone (m. p. 153°) is boiled for ten hours with dilute hydrochloric acid, it is converted into a *γ-ketonic acid*, $CH_2{:}O_2{:}C_6H_3{\cdot}CO{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, which forms pale yellow, prismatic crystals melting at 157°; if the boiling is only continued for five hours, an unsaturated *lactone*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{<}\begin{matrix}CPh{:}CH\\ O{-\!-}CO\end{matrix}$ or

$$CH_2{:}O_2{:}C_6H_3{\cdot}C{<}\begin{matrix}CPh{\cdot}CH_2\\ O{-\!-}CO\end{matrix},$$

is produced, crystallising in leaflets melting at 183°. The same lactone is also produced when the insoluble lactone (m. p. 205°) is reduced with zinc and acetic acid; at the same time, an unsaturated *acid*,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CPh{\cdot}CH(OH){\cdot}CO_2H,$$

is obtained as a crystalline powder melting at 147°. When boiled with hydrochloric acid, this acid yields both the unsaturated lactone (m. p. 183°) and the γ-ketonic acid (m. p. 157°) just described.

Phenylpyruvic acid condenses with cinnamaldehyde forming an *a-oxylactone*, $CHPh{:}CH{\cdot}CH{<}\begin{matrix}CHPh{\cdot}CO\\ O{-\!-\!-}CO\end{matrix}$, which crystallises in needles melting at 179°. No definite substance was isolated from the condensation product of furfuraldehyde and phenylpyruvic acid.

K. J. P. O.

a Oxy-β-phenyl-γ-methoxyphenylbutyrolactone and its Transformations. EMIL ERLENMEYER, jun., and A. LATTERMANN (*Annalen*, 1904, 333, 268—276).—Phenylpyruvic acid and anisaldehyde yield the *a-oxy-β-phenyl-γ-methoxyphenylbutyrolactone*,

$$OMe{\cdot}C_6H_4{\cdot}CH{<}\begin{matrix}CHPh{\cdot}CH{\cdot}OH\\ O{-\!-\!-}CO\end{matrix},$$

which forms crystals melting at 191°. The *benzoyl* derivative forms needles melting at 170°, and the *acetyl* derivative aggregates of needles melting at 116°. When heated above its melting point until gas ceases to be evolved, the lactone is converted into *p*-methoxystilbene, $CHPh{:}CH{\cdot}C_6H_4{\cdot}OMe$, which crystallises in colourless leaflets melting at 135°; its *dibromide* melts at 177° and loses bromine on recrystallisation.

On reduction with sodium amalgam, the a-oxy-lactone is converted into two isomeric substances: a sparsely soluble *substance* melting at 155° and a readily soluble *compound* melting at 123°; both are

neutral, and are probably α-hydroxy-lactones,

$$OMe\cdot C_6H_4\cdot CH<\begin{matrix} CHPh\cdot CH\cdot OH \\ O\text{———}CO \end{matrix}.$$

The *acetyl* derivative of the hydroxy-lactone (m. p. 123°) crystallises in needles melting at 117°. When boiled with hydrochloric acid, the hydroxy-lactone is converted into the corresponding γ-ketonic acid, $OMe\cdot C_6H_4\cdot CO\cdot CHPh\cdot CH_2\cdot CO_2H$, which forms crystals melting at 148°.

When reduced with zinc dust and acetic acid, the α-oxy-lactone yields but small quantities of the unsaturated acid,

$$OMe\cdot C_6H_4\cdot CH\colon CPh\cdot CH(OH)\cdot CO_2H,$$

which melts at 145°, but is mainly converted into two unsaturated lactones melting respectively at 122° and 105°; the lactone melting at 105° is transformed into that melting at 122° by prolonged heating with acetic anhydride or by the action of an alcoholic solution of aniline. Both lactones are converted into the γ-ketonic acid (m. p. 148°) by heating with sodium hydroxide. When condensed with benzaldehyde, both lactones yield the *compound*

$$OMe\cdot C_6H_4\cdot C\lessgtr\begin{matrix} CPh\cdot C\colon CHPh \\ O\text{----}CO \end{matrix},$$

which crystallises in orange-yellow needles melting at 195°; hence the lactones are represented by the formula $OMe\cdot C_6H_4\cdot C\lessgtr\begin{matrix} CPh\cdot CH_2 \\ O\text{----}CO \end{matrix}$.

K. J. P. O.

α-Oxy-β-phenyl-γ-benzylbutyrolactone and its Transformations. Emil Erlenmeyer, jun., and E. Reis (*Annalen*, 1904, **333**, 276—283).—α-Oxy-β-phenyl-γ-butyrolactone is reduced by 4 per cent. sodium amalgam to two stereoisomeric *hydroxy-lactones*,

$$CH_2Ph\cdot CH<\begin{matrix} CHPh\cdot CH\cdot OH \\ O\text{———}CO \end{matrix},$$

which are separated by crystallisation from chloroform; the more sparingly soluble compound forms crystals melting at 153°, whilst the more easily soluble crystallises in needles melting at 113°. Both are unchanged by boiling with 20 per cent. hydrochloric acid, and both yield the same *acetyl* derivative on treatment with acetic anhydride; the latter crystallises in needles melting at 142° and is converted on hydrolysis into the hydroxy-lactone (m. p. 153°). When reduced with zinc dust and acetic acid, the oxy-derivative is converted into the hydroxylactone (m. p. 153°) and into an unsaturated *acid*,

$$CH_2Ph\cdot CH\colon CPh\cdot CH(OH)\cdot CO_2H,$$

crystallising in needles melting at 128°; by boiling with hydrochloric acid, it is transformed into the isomeric ketonic acid,

$$CH_2Ph\cdot CO\cdot CHPh\cdot CH_2\cdot CO_2H,$$

which melts at 128°.

Since it was possible that in the reduction of the α-oxy-lactone α-hydroxy-lactone was formed as an intermediate product, which then was converted into unsaturated acids, an attempt was made to obtain the unsaturated acid from the α-hydroxy-lactone (m. p. 153°) by prolonged boiling with zinc acetate and acetic acid. The hydroxy-lactone

was recovered unchanged; hence the hydroxy-lactone is a by-product and not an intermediate stage. K. J. P. O.

Conversion of Piperidine into Pentamethylenediamine (Cadaverine). JULIUS VON BRAUN (*Ber.*, 1904, 37, 3583—3588).—Benzoylpiperidine yields $\alpha\epsilon$-dichloropentane with phosphorus chloride (this vol., i, 918). This may then be combined with phthalimide, and the product yields pentamethylenediamine (cadaverine) on hydrolysis.

Pentamethylenediphthalimide,

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot[CH_2]_5\cdot N{<}{}^{CO}_{CO}{>}C_6H_4,$$

prepared by heating crude dichloropentane (containing benzonitrile) with potassium phthalimide at 200°, crystallises from alcohol and chloroform in long, felted, slightly yellow needles and melts at 186°. It dissolves sparingly in solvents with the exception of hot chloroform. It dissolves in potassium hydroxide solution, and acids then precipitate *pentamethylenediphthalamic acid*, $C_5H_{10}(NH\cdot CO\cdot C_6H_4\cdot CO_2H)_2$, which is difficult to purify, but may be precipitated from its alcoholic solution by ether as a white, crystalline powder, melting and decomposing into water and the phthalimide at 156°.

Concentrated hydrochloric acid hydrolyses the phthalimide at 200° to pentamethylenediamine, $NH_2\cdot[CH_2]_5\cdot NH_2$, which is identified by means of its salts. The *benzenesulphonyl* derivative, $C_5H_{10}(NH\cdot SO_2Ph)_2$, separates from alcohol in colourless, glistening crystals and melts at 119°. C. H. D.

Formyl-*p*-aminophenylglycine. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 154556).—Formylphenylglycine may be nitrated in the same manner as acetylphenylglycine (this vol., i, 806).

Formyl-p-*nitrophenylglycine* crystallises from glacial acetic acid in brownish-yellow tablets, melts and decomposes at 159—160°, and dissolves in alkalis to a pale yellow solution. *Formyl*-p-*aminophenylglycine*, obtained by reduction, is very soluble in water and has not been isolated in the solid state. Its diazonium compounds may be employed for the preparation of dyes. C. H. D.

Preparation of Indigotin. KALLE & Co. (D.R.-P. 154524).—Sulphophenylglycinecarboxylic acid is converted into indigo-white by fusion with sodamide. The temperature required is lower than when alkali hydroxides are employed, the removal of the sulpho-group being complete at 200—220°. C. H. D.

Bromination of Indigotin. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 154511. Compare this vol., i, 57, 167).—In the bromination of indigotin in sulphuric acid solution, the acid may be employed of as low a strength as 40 per cent., or even less if a limited quantity is used. A large excess of dilute sulphuric acid, however, causes the formation of bromoisatin. The bromoindigotin prepared in this way is identical with that obtained by dry bromination.

C. H. D.

Brominated Homologues of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 154338. Compare this vol., i, 57, 167).—The homologues of indigotin may be brominated in the presence of mineral acids. The products contain the bromine in the nucleus, and form blue powders with coppery lustre, dissolving fairly readily in organic solvents. *Bromo-* and *dibromo-*o-*tolylindigotin* and *bromo-* and *dibromo-*m-*xylylindigotin* are described. C. H. D.

Compounds from Lichens. XII. WILHELM ZOPF (*Annalen*, 1904, 336, 46—85. Compare Abstr., 1895, i, 297; 1896, i, 103; 1897, i, 362, 436; 1898, i, 89, 489; 1899, i, 716; 1901, i, 87, 546; 1902, i, 465, 788; 1903, i, 762).—*Lepranthra impolita* (*Arthonia pruinosa*) has been obtained from an oak barn door at Eckern in Oldenburg. The dark olive-green ethereal extract contains lecanoric acid, lepranthin, and lepranthaic acid.

Lepranthin, $C_{25}H_{40}O_{10}$, crystallises in thin, colourless, monoclinic plates [$a:b:c = 2\cdot4017:1:0\cdot9273$; $\beta = 16°57'40''$], melts at 183°, has $[\alpha]_D + 71°$ at 17°, and is easily soluble in alcohol, ether, or benzene, but only slightly so in light petroleum; the alcoholic solution has a neutral reaction and gives no coloration with ferric chloride.

Lepranthaic acid, $C_{20}H_{32}O_2$, crystallises in quadratic plates, melts at 111—112°, is moderately soluble in ether, alcohol, or hot benzene, and dissolves easily in sodium hydrogen carbonate solution, from which it is reprecipitated on addition of hydrochloric acid; its solutions in aqueous alkali hydroxides lather like soap solutions; it is not changed when heated with absolute alcohol in a sealed tube for three quarters of an hour at 155—160°.

Evernia illyrica, obtained from Dalmatia and Istria, contains 5·5 per cent. of divaricatic acid and almost 0·5 per cent. of atranoric acid, but neither usnic nor evernic acids.

The yellow colour of *Pertusaria Wulfenii* (*P. sulfurea*, *P. sulphurella*, *P. fallax*, &c.), as of *P. lutescens* (Abstr., 1901, i, 547), is due to the presence of thiophanic acid. The extract contains also a small amount of a white, crystalline *substance*.

Diploïcia canescens (*Catolechia canescens*; *Buellia canescens*), obtained from the sandstone walls of a castle in Bentheim, Westphalia, was partly sterile. When washed with aqueous sodium hydrogen carbonate solution, the ethereal solution yields a crystalline precipitate of diploicin (0·75 per cent.) and catolechin (0·01 per cent.); on evaporation of the ethereal filtrate, atranoric acid (0·3 per cent.) and a small amount of an amorphous, brown powder insoluble in benzene are obtained.

Diploicin forms sheaves of brown, thick crystals, melts at 225°, is only slightly soluble in alcohol, ether, glacial acetic acid, or benzene, has only a slight tendency to redden litmus paper, and gives no coloration with ferric chloride.

Catolechin crystallises in long, slender, white needles, softens at 210°, melts at 214—215°, is slightly more soluble in benzene than is diploicin, does not redden litmus paper, and gives no coloration with ferric chloride. Diploicin and catolechin are insoluble in aqueous alkali hydroxides or in concentrated sulphuric acid.

Phlyctis argena, from ash trees in Oldenburg, contains salazinic acid.

Cetraria nivalis contains usnic acid, but no protolichesteric, protocetraric, nor cetraric acid.

Cetraria stuppea, from Lengerich in Westphalia, contains protolichesteric acid and a *substance* which forms granular crystals, melts at 197—198°, and is not soluble in aqueous sodium hydrogen carbonate solution.

Contrary to Hesse's statement (Abstr., 1902, i, 68), *Cetraria aculeata* (*Cornicularia aculeata*) contains protolichesteric acid and no rangiformic acid.

Cladonia squamosa (var. *ventricosa*), obtained from granite blocks in Achtermann, Oberharz, contains squamatic acid (Hesse, Abstr., 1901, i, 150) and usnic acid.

Xanthoria lychnea, var. *pygmæa* (*X. candelaria*; *X. controversa*; *X. parietina*, var. *lychnea*) was gathered from old beams of sennhuts at the Ferrare Alpe on the Grödener Joch and from the Regensburger Hutt. It contains parietin (1·5 per cent.), which crystallises in orange-coloured, slender needles and melts at 202°, but not chrysophanic acid, which melts at 162°.

The occurrence of parietin in *Gasparrinia elegans* (*Amphiloma elegans*; *Placodium elegans*; *Physcia elegans*) (Thompson, *Annalen*, 1845, 53, 266) is confirmed; no rhizocarpic acid could be detected.

Lecidea aglæotera (*L. armeniaca*, var. *lutescens*) contains roccellic acid ($6\frac{1}{2}$ per cent.) and cetraric acid (0·9 per cent.).

Contrary to Hesse's statement (Abstr., 1901, i, 149), *Usnea florida* contains usnic acid, hirtellic acid, and a *substance* which crystallises in spherical aggregates of needles, melts at about 200°, dissolves in sodium hydroxide solution or concentrated sulphuric acid with an intense yellow colour, but neither usnaric, atranoric, nor hirtic acid.

G. Y.

Purification of Aromatic Aldehydes. Chemische Fabrik Griesheim-Elektron (D.R.-P. 154499).—Sulphurous acid may be employed for the purification of aromatic aldehydes instead of alkali hydrogen sulphites, as it readily dissolves aldehydes, leaving the hydrocarbons and other impurities undissolved. No alkali is needed to decompose the solution, gentle heating at 100° or the passage of a current of air being sufficient to expel the sulphur dioxide. Potassium chloride precipitates the potassium hydrogen sulphite compounds from the solution.

C. H. D.

Oxidising Chlorination of *o*- and *p*-Hydroxybenzaldehydes. Heinrich Biltz (*Ber.*, 1904, 37, 4003—4010. Compare Abstr., 1902, i, 162).—The action of chlorine on *p*-hydroxybenzaldehyde in acetic acid solution at 100° leads to the formation of α-heptachloroketotetrahydrobenzene, $CCl_2<\substack{CHCl\cdot CCl_2 \\ CCl=CCl}>CO$ (Zincke, Abstr., 1894, i, 231), on salicylaldehyde, to the formation of α-heptachloroketotetrahydrobenzene and chloranil. If the chlorination is carried out in anhydrous acetic acid solution, or at 50—55°, dichlorosalicylaldehyde

is formed, at 80°, at first *dichlorosalicylaldehyde*, and, after eight hours, a small amount of the heptachloroketone are formed. When heated to 180°, the heptachloroketone loses 1 mol. of hydrogen chloride and forms hexachloroketodihydrobenzene; at temperatures above 200°, perchlorophenylene oxide, $(C_6Cl_4O)_x$, which melts at 325—326°, is formed.

α-Heptachloroketotetrahydrobenzene is easily reduced by stannous chloride and hydrochloric acid to pentachlorophenol, which melts at 190—191°. When warmed with concentrated nitric acid, the heptachloroketone yields chloranil (compare this vol., i, 1000, and following abstracts). G. Y.

Chlorination of Salicylaldehyde. HEINRICH BILTZ and KARL STEPF (*Ber.*, 1904, 37, 4022—4031. Compare foregoing abstract).—5-Chlorosalicylaldehyde (Bradley and Dains, Abstr., 1892, 1458; Visser, Abstr., 1898, i, 202) is obtained by the action of chlorine on salicylaldehyde warmed on the water-bath. The *phenylhydrazone*, $C_{16}H_{11}ON_2Cl$, crystallises in long, flesh-coloured needles and melts at 148°; the *semicarbazone*, $C_8H_8O_2N_3Cl$, crystallises in long, white needles and melts and decomposes at 286—287°. When boiled with acetic anhydride, the oxime yields 5-*chloro*-2-*acetoxybenzonitrile*, $OAc\cdot C_6H_3Cl\cdot CN$, which crystallises in thick, white, transparent needles and melts at 79—80°. 5-*Chlorosalicylonitrile* crystallises in thin, brown needles and melts at 165—167°; 5-chloro-2-hydroxybenzamide crystallises in small, white leaflets and melts at 226—227° (compare Smith, *Ber.*, 1878, 11, 1227). The acid, obtained on hydrolysis of the nitrile, crystallises in small, white needles and melts at 168°. When heated with concentrated sulphuric acid, the nitrile yields *p*-chlorophenol.

3:5-Dichlorosalicylaldehyde, $OH\cdot C_6H_2Cl_2\cdot COH$, is formed when salicylaldehyde is persistently chlorinated in anhydrous acetic acid or chloroform solution at 100°; it crystallises in yellow prisms, melts at 95°, is easily soluble in the usual organic solvents, forms yellow *sodium* and *ammonium* derivatives, and is decomposed by warm concentrated sulphuric or nitric acids. The *phenylhydrazone* crystallises in yellow, rhombic plates and melts at 153°; the *semicarbazone* crystallises in silky, yellow needles and melts at 227°; the *oxime* crystallises in colourless, silky needles and melts at 195—196°. 3:5-*Dichloro*-2-*acetoxybenzonitrile*, formed by boiling the oxime with acetic anhydride, crystallises in long needles and melts at 78°; 3:5-*dichlorosalicylonitrile* forms short needles and melts at 139°. 3:5-Dichlorosalicylic acid melts at 219° (Zincke and Walbaum, Abstr., 1891, 708). When heated with concentrated hydrochloric acid in a sealed tube at 250°, 3:5-dichloro-2-acetoxybenzonitrile yields *o*-*p*-dichlorophenol. G. Y.

***m*-Chloro-*p*-hydroxybenzaldehyde.** HEINRICH BILTZ (*Ber.*, 1904, 37, 4031—4036. Compare foregoing abstracts).—m-*Chloro*-p-*hydroxybenzaldehyde* is formed by the action of chlorine (1 mol.) on *p*-hydroxybenzaldehyde (1 mol.) in an ice-cooled saturated chloroform solution. It crystallises in long, white, slender needles, melts at 139°, and boils at 149—150° under 14 mm. pressure (compare Peratoner and Ortoleva, Abstr., 1898, i, 643). The *semicarbazone* crystallises

in long, slender, yellow needles and melts and decomposes at 210°; the *oxime* crystallises in long, white needles and melts at 144—145°; the *acetate* of the nitrile, $OAc\cdot C_6H_3Cl\cdot CN$, crystallises in colourless leaflets and melts at 89—90°. m-*Chloro*-p-*hydroxybenzonitrile* crystallises in white needles and melts at 155°; m-*chloro*-p-*hydroxybenzamide* crystallises in needles and melts at 176—178°; *m*-chloro-*p*-hydroxybenzoic acid melts at 169° (Lössner, this Journal, 1876, ii, 282). *mm*-Dichloro-*p*-hydroxybenzaldehyde (Auwers and Reis, Abstr., 1897, i, 53) melts at 158—159°; the *semicarbazone* crystallises in matted, green needles and melts and decomposes at 236—237°. G. Y.

Behaviour of *N*-Alkyl Aldoximes towards Benzenesulphonic Chloride, Phthalyl Chloride, and Picryl Chloride. ERNST BECKMANN [and R. DÜTSCHKE] (*Ber.*, 1904, 37, 4136—4139).—*N*-Benzylbenzaldoxime is converted by the action of benzenesulphonic chloride in benzene solution at water-bath temperature into benzylbenzamide; in addition, ammonium benzenesulphonate and *tribenzylamine benzenesulphonate* are formed in small quantity; the latter forms glistening needles melting at 200°. In alkaline solution, benzylaldoxime is converted almost entirely into benzylbenzamide. From *N*-benzylanisaldoxime, either in benzene or alkaline solution, benzylanisamide was formed by the action of either benzenesulphonic, phthalyl, or picryl chlorides. These results are interpreted as showing that the rearrangement of oximino-compounds to amides is in the main an instance of catalytic change. E. F. A.

Action of Magnesium Ethyl Iodide on Piperonaldehyde. New Synthesis of *iso*Safrole. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 315—323. Compare this vol., i, 668).—The action in the cold of magnesium ethyl iodide (1 mol.) in ethereal solution on piperonaldehyde leads to the formation of ethylpiperonyl alcohol, which, when heated, loses a molecule of water yielding *iso*safrole. On oxidising ethylpiperonyl alcohol by means of chromic acid, it gives piperonyl ethyl ketone (propiopiperone), the constitution of which must hence be $CH_2{:}O_2{:}C_6H_3\cdot COEt$ (compare Wallach and Pond, Abstr., 1896, i, 94).

Ethylpiperonylcarbinol [α-3 : 4-*methylenedioxyphenylpropyl alcohol*], $CH_2<\begin{matrix}O\cdot C\cdot CH{:}CH\\ O\cdot C\cdot CH{:}C\cdot CHEt\cdot OH\end{matrix}$, is an oily liquid which boils at 172—175° under 20 mm. pressure, has a faint odour recalling that of *iso*safrole, and is soluble in benzene, ether, chloroform, alcohol, acetic acid, or pyridine; it has a sp. gr. 1·189 at 0°/15°. It has the normal molecular weight in freezing benzene, and, on boiling, decomposes into water and the corresponding unsaturated hydrocarbon. Its *acetyl* derivative, $CH_2{:}O_2{:}C_6H_3\cdot CHEt\cdot OAc$, is a white, oily liquid with a faint pleasant acetic odour and boils at 182—185° under 12 mm. pressure.

*Chlorodihydro*iso*safrole* [α-*chloro*-α-3 : 4-*methylenedioxyphenylpropane*], $CH_2<\begin{matrix}O\cdot C\cdot CH{:}CH\\ O\cdot C\cdot CH{:}C\cdot CHEtCl\end{matrix}$, prepared by passing dry hydrogen chloride into a cold ethereal solution of piperonylethylcarbinol, is an

unstable, oily liquid not capable of being purified by distillation. It combines with pyridine, giving a *compound* separating in tufts of straw-yellow crystals; the *platinichloride* of this compound,

$$(CH_2:O_2:C_6H_3\cdot CHEt\cdot C_5NH_5Cl)_2,PtCl_4,$$

begins to turn brown at 170° and melts and decomposes at 180—185°; the *aurichloride*, $CH_2:O_2:C_6H_3\cdot CHEt\cdot C_5NH_5Cl,AuCl_3$, blackens at 135° and melts and decomposes at 140—145°. T. H. P.

Compounds of Unsaturated Ketones with Metallic Chlorides. ARTHUR ROSENHEIM and WALTER LEVY (*Ber.*, 1904, **37**, 3662—3671).—Cinnamaldehyde, when mixed with antimony chloride in chloroform solution, forms a compound, $C_9H_8O,SbCl_5$, crystallising in glistening, colourless crystals; with tin chloride, a citron-yellow, crystalline compound, $2C_9H_8O,SnCl_4$, is obtained; the corresponding tin bromide compound melts at 186°. Ethyl cinnamate forms stable compounds, $3C_{11}H_{12}O_2,2SbCl_5$; $2C_{11}H_{12}O_2,SnCl_4$; $C_{11}H_{12}O_2,FeCl_3$; whilst from cinnamic acid, the compounds $3C_9H_8O_2,2SbCl_5$, which forms orange-yellow crystals, $2C_9H_8O_2,SnCl_4$, faintly red-coloured crystals, and $C_9H_8O_2,FeCl_3$, bright yellow, hygroscopic needles, are obtained, chloroform being in each case employed as a solvent. Dibenzylideneacetone forms a crystalline compound, $C_{17}H_{14}O,SbCl_5,HCl$, and also compounds, $C_{17}H_{14}O,SnCl_4,HCl$, large cinnabar-red plates;

$$C_{17}H_{14}O,FeCl_3,$$

blackish-green needles, and $C_{17}H_{14}O,SnBr_4$, bright red crystals. Cinnamylideneacetophenone forms a blackish-violet, crystalline powder, $C_{17}H_{14}O,SbCl_5,HCl$, which dissolves in chloroform giving a deep violet solution with a red lustre. The tin chloride compound,

$$C_{17}H_{14}O,SnCl_4,HCl,$$

shows a blue, inky coloration in chloroform and forms a blood-red ethereal solution. The iron compound, $C_{17}H_{14}O,2FeCl_3$, separates in black crystals from a deep brown solution. Benzylidenecinnamylideneacetone forms a blackish-green, crystalline powder,

$$C_{19}H_{16}O,SbCl_5,HCl;$$

the tin salt, $C_{19}H_{16}O,SnCl_4,HCl$, separates in dark blue crystals from the deep red chloroform solution. Dicinnamylideneacetone forms an iron compound, $C_{21}H_{18}O,2FeCl_3$, separating from the purplish-red chloroform solution in blackish-green crystals. From these results, the authors draw the conclusion that the tendency of unsaturated compounds containing oxygen to form additive compounds is due to the oxygen, and that the activity of the oxygen is increased by the presence of doubly-linked carbon atoms in the molecule. E. F. A.

Addition of Alkali Hydrogen Sulphites and of Sulphurous Acid to Unsaturated Compounds. EMIL KNOEVENAGEL (*Ber.*, 1904, **37**, 4038—4059. Compare Tiemann, Abstr., 1899, i, 247; Harries, this vol., i, 427)—[With ERNST REINECKE].—When shaken with a freshly prepared aqueous solution of sulphur dioxide, dimethyl*cyclo*hexenone forms an *additive* compound, which, on evaporation, is obtained as a viscid oil, which gradually becomes yellow. If the aqueous solution is neutralised with sodium carbonate before evapora-

tion, the *sodium* salt, $CH_2<\begin{smallmatrix}CHMe\cdot CH_2\\CO——CH_2\end{smallmatrix}>CMe\cdot SO_3Na$, is obtained as a white, crystalline mass. The *additive* compound of 1-methyl-3-phenyl-Δ^3-*cyclo*hexene-5-one, and sulphurous acid forms the barium salt, $(C_6H_7MePh\cdot SO_3)_2Ba$, which crystallises in large prisms.

[With Erich Lange.]—The *additive* compound, formed on shaking carvone with an 8 per cent. aqueous solution of sulphurous acid, yields the *sodium* salt, $\begin{array}{l}CH_2{:}CMe\cdot CH\cdot CH_2\cdot CH\cdot SO_3Na\\ \qquad\qquad\;\; CH_2\cdot CO-CHMe\end{array}$ (?). This is obtained on evaporation as a viscid, yellow oil, which solidifies in a desiccator to a yellow, crystalline, hygroscopic mass; it is easily soluble in water or alcohol, but insoluble in ether. The *barium* salt crystallises in monoclinic leaflets.

[With Edmund Speyer.]—The *additive* compound obtained from ethyl ethylideneacetoacetate and sulphurous acid forms a *sodium* salt which crystallises in small needles and a crystalline *barium* salt. Benzylideneacetone dissolves only slowly (24 hours) in aqueous sulphurous acid; the *sodium* salt of the additive compound is very soluble in water; the *barium* salt and *potassium* salt, $C_{10}H_{11}O_4SK$, are crystalline; on addition of sodium hydroxide, the potassium salt yields benzylideneacetone.

[With R. Morisse.]—Cinnamaldehyde dissolves in 5 per cent. aqueous sulphurous acid (30 minutes) to a yellow solution; the *additive* compound so formed is decomposed when warmed or on addition of alkali hydroxides or carbonates. The sodium salt, formed on addition of sodium acetate, crystallises in glistening leaflets and is identical with the additive compound of cinnamaldehyde and sodium hydrogen sulphite; with phenylhydrazine acetate in aqueous solution, it forms the phenylhydrazone of cinnamaldehyde. The action of aqueous sulphurous acid on cinnamaldehyde for 8—10 days leads to the formation of the *additive* compound,

$$SO_3H\cdot CHPh\cdot CH_2\cdot CH(OH)\cdot SO_3H,$$

which is more stable than the compound with 1 mol. of sulphurous acid; the *barium* salt, $C_9H_{10}O_7S_2Ba,3H_2O$, is crystalline (compare Heusler, Abstr., 1891, 1051). When warmed with dilute sulphuric acid and treated with barium carbonate, the additive compound of cinnamaldehyde and 2 mols. of sulphurous acid yield *barium cinnamaldehydesulphonate*, $(COH\cdot CH_2\cdot CHPh\cdot SO_3)_2Ba,2H_2O$, which is hygroscopic. If a freshly prepared aqueous solution of cinnamaldehyde and sulphurous acid is treated with sodium hydroxide, a stable *sodium* salt, $CHPh{:}CH\cdot CH(OH)\cdot SO_3Na$(?), is formed, isomeric with Heusler's salt and with cinnamaldehyde sodium hydrogen sulphite.

When shaken with aqueous sulphurous acid for 8—10 hours, phorone forms an *additive* compound with 2 mols. of sulphurous acid; the sodium salt is identical with the additive compound of phorone and sodium hydrogen sulphite; the *barium* salt, $C_9H_{16}O_7S_2Ba,4H_2O$, crystallises in thick needles.

Allylacetone combines with 1 mol. of sulphurous acid; the *sodium* salt and the *barium* salt, $C_{12}H_{22}O_8S_2Ba,H_2O$, do not yield allylacetone when warmed with aqueous sodium hydroxide, the molecule of sulphurous

acid is therefore probably added to the ethylene linking and not to the carbonyl.

Benzylideneacetophenone does not react with aqueous sulphurous acid; with potassium hydrogen sulphite it forms the *potassium* salt, $C_{15}H_{13}O_4SK$, which crystallises in thick, white needles and yields benzylideneacetophenone when treated with sodium hydroxide or when heated to 155°.

Piperonylideneacetonehydrosulphonic acid, formed when piperonylideneacetone is shaken with aqueous sulphurous acid for 40 hours, is stable in aqueous solution; on concentration, it decomposes to a dark gum-like mass, and on addition of sodium hydroxide yields piperonylideneacetone. The *sodium* salt, $C_{11}H_{11}O_6SNa,2H_2O$, crystallises in clusters of needles; the *barium* salt, $C_{22}H_{22}O_{12}S_2Ba$, crystallises from dilute alcohol. Piperonylideneacetone dissolves easily in boiling aqueous potassium hydrogen sulphite, forming the *potassium* salt, $C_{11}H_{11}O_6SK,H_2O$.

p-Methoxybenzylideneacetone dissolves in cold aqueous sulphurous acid to a yellow solution which deposits the ketone when warmed on the water-bath; the *sodium* salt, $C_{11}H_{13}O_5SNa,H_2O$, crystallises in small, white needles; the *potassium* salt, $C_{11}H_{13}O_5SK,H_2O$, formed by dissolving the ketone in boiling aqueous potassium hydrogen sulphite, crystallises in small needles.

Cinnamylideneacetone dissolves only slowly in aqueous sulphurous acid (60 hours); the *sulphonic acid* is stable towards alkali carbonates or acids, but is decomposed, with formation of the ketone, on addition of potassium hydroxide. The *barium* salt, $C_{24}H_{26}O_8S_2Ba,8H_2O$, forms thick crystals and loses 6—$7H_2O$ at 100°.

Benzylidenecinnamylideneacetone dissolves only in traces in aqueous sulphurous acid; with aqueous potassium hydrogen sulphite it forms the *potassium* salt of the *bishydrosulphonic acid*, $C_{19}H_{18}O_7S_2K_2,3H_2O$, which is easily soluble in water and yields the ketone when treated with sodium hydroxide.

Dibenzylideneacetone is insoluble in aqueous sulphurous acid; with aqueous potassium hydrogen sulphite, it forms the *potassium* salt, $C_{17}H_{16}O_7S_2K_2,3\frac{1}{2}H_2O$, which crystallises in slender needles and yields the ketone when treated with sodium hydroxide or concentrated aqueous potassium carbonate solution.

Dipiperonylideneacetone is best prepared by treating piperonal with acetone and concentrated aqueous sodium hydroxide in alcoholic solution; it melts at 185°, is only slightly soluble in aqueous sulphurous acid after 90 hours. The *barium* salt, $C_{19}H_{14}O_{11}S_2Ba$, is obtained by addition of barium carbonate to the solution of the ketone in aqueous sulphurous acid; the *potassium* salt, $C_{19}H_{14}O_{11}S_2K_2,2\frac{1}{2}H_2O$, is obtained by heating the ketone with aqueous potassium hydrogen sulphite, and yields the ketone when treated with sodium hydroxide.

Dicuminylideneacetone is only slightly soluble in aqueous sulphurous acid; even after shaking for 90 hours, only a very small amount of the *barium* salt, $C_{23}H_{28}O_7S_2Ba,3H_2O$, is obtained on treatment with barium carbonate. Dicuminylideneacetone reacts with potassium hydrogen sulphite, more slowly than the foregoing ketones, to form the *potassium* salt, $C_{23}H_{28}O_7S_2K_2,3H_2O$, which yields the ketone on treat-

ment with sodium hydroxide or concentrated aqueous potassium carbonate. The potassium salt, $C_{23}H_{28}O_7S_2K_2,1\frac{1}{2}H_2O$, was obtained once on recrystallisation from alcohol.

When boiled with aqueous potassium hydrogen sulphite, benzylidene-furfurylideneacetone forms the potassium salt, $C_{15}H_{14}O_8S_2K_2,2H_2O$, which is decomposed on treatment with sodium hydroxide or aqueous potassium carbonate.

Ethyl ethylidenemalonate dissolves completely in aqueous sulphurous acid; the resulting *hydrosulphonic acid* is stable in aqueous solution, and on evaporation in a vacuum is obtained as a viscid syrup which gradually decomposes, becoming brown. The *barium* salt,

$$C_{18}H_{30}O_{14}S_2Ba,$$

is yellow and deliquesces on exposure to moist air; the *potassium* salt, $C_9H_{15}O_7SK$, is formed by the action of aqueous potassium hydrogen sulphite on the ester.

Ethyl cinnamate is insoluble in aqueous sulphurous acid; with aqueous potassium hydrogen sulphite, it forms the *potassium* salt, $C_{11}H_{13}O_5SK,1\frac{1}{2}H_2O$, which crystallises in white needles and is hydrolysed to cinnamic acid when boiled with aqueous sodium hydroxide.

Ethyl benzylidenemalonate and potassium hydrogen sulphite, in boiling aqueous solution, form the *potassium* salt, $C_{14}H_{17}O_7SK,1\frac{1}{2}H_2O$, from which about 15 per cent. of the ester is obtained on treatment with aqueous sodium hydroxide.

When boiled with aqueous potassium hydrogen sulphite, ethyl cuminylidenemalonate forms the *potassium* salt, $C_{17}H_{23}O_7SK,\frac{1}{2}H_2O$, from which about 18 per cent. of the ester is obtained on treatment with aqueous sodium hydroxide. G. Y.

Action of Potassium Cyanide on the Additive Compounds of Alkali Hydrogen Sulphites and Unsaturated Compounds. EMIL KNOEVENAGEL and ERICH LANGE (*Ber.*, 1904, 37, 4059—4065. Compare foregoing abstract).—When heated with a concentrated aqueous solution of potassium cyanide, sodium 1 : 3-dimethyl*cyclo*hexene-(3)-one-5-hydrosulphonate yields 1-*cyano*-1 : 3-*dimethyl*cyclo*hexane-5-one*, $CH_2<\begin{matrix}CO——CH_2\\CHMe\cdot CH_2\end{matrix}>CMe\cdot CN$, which crystallises in plates or long, thin needles, and melts at 92—94°. The *semicarbazone*, $C_{10}H_{16}ON_4$, crystallises in nacreous leaflets and melts at 200—201°. The *carboxylic acid*, $C_6H_7OMe_2\cdot CO_2H$, crystallises with water of crystallisation, sinters at 87°, and melts at 105—120°, or when anhydrous at 124—125°; it is easily soluble in alcohol, ether, warm benzene, or warm water.

Prolonged heating of sodium 1 : 3-dimethyl*cyclo*hexenone with aqueous potassium cyanide leads to the formation of a *substance*, $C_{10}H_{15}O_3N,2H_2O$, which melts at 204°, loses $2H_2O$ at 210°, and, when anhydrous, crystallises in colourless needles, melts at 220—221°, and is the cyanohydrin of dimethyl*cyclo*hexanonecarboxylic acid,

$$\begin{matrix}CN\cdot C(OH)\cdot CH_2\cdot CMe\cdot CO_2H\\ \quad | \qquad\qquad\qquad | \\ CH_2\cdot CHMe\text{-}CH_2\end{matrix},$$

or the imide of 1 : 5-dimethyl-3-hydroxyhexahydro*iso*phthalic acid,

$$CHMe\left\langle\begin{array}{l}CH_2\cdot CMe—CO\\ \qquad\quad >CH_2\\ CH_2\cdot C(OH)—CO\end{array}\right\rangle NH.$$

The *dicarboxylic acid*, $C_8H_8O(CO_2H)_2$, crystallises from dilute alcohol, and melts at 165—170°, or when anhydrous, at 182—183°. G. Y.

Formation of Additive Compounds of Hydrogen Cyanide and Unsaturated Compounds. EMIL KNOEVENAGEL (*Ber.*, 1904, 37, 4065—4073. Compare foregoing abstracts ; Bredt and Kallen, Abstr., 1897, i, 154 ; Lapworth, Trans., 1903, 83, 999)—[With KARL SCHLEUSSNER].—When boiled with potassium cyanide in aqueous-alcoholic solution, α-phenylcinnamonitrile yields diphenylsuccinonitrile and a *substance*, $C_{16}H_{13}O_2N$, which forms white crystals, melts at 196—198°, is soluble in aqueous alkali hydroxides, and is either diphenylsuccinimide or αβ-diphenyl-β-cyanopropionic acid, as it is hydrolysed to diphenylsuccinic acid by boiling alcoholic potassium hydroxide.

[With P. SCHLÜCHTERER.]—α-Phenylcinnamonitrile and hydrogen cyanide, in ethereal solution at the ordinary temperature, formed only traces of diphenylsuccinonitrile in 14 days. The reaction is accelerated by the addition of organic bases, as in 8 days 1 gram of diphenylsuccinonitrile was formed from 5 grams of α-phenylcinnamonitrile and hydrogen cyanide in presence of diethylamine or piperidine in ethereal solution. In presence of ethylamine, 0·8 gram, of amylamine, 0·3 gram, and of quinoline, 0·1 gram of the product was obtained. When heated at 100° for $2\frac{1}{2}$ hours, 5 grams of α-phenylcinnamonitrile and hydrogen cyanide in alcoholic solution formed 1·6 grams of diphenylsuccinonitrile; under the same conditions, but with addition of piperidine, 2·1 grams of product were obtained.

The action of hydrogen cyanide on ethyl benzylideneacetoacetate in presence of piperidine, and hydrolysis of the product leads to the formation of phenylsuccinic acid. The piperidine may be replaced by diethylamine, methylamine hydrochloride, or potassium carbonate.

Hydrogen cyanide reacts with benzylideneacetone only in presence of organic bases. The product could not be purified or hydrolysed.

Mesityl oxide and hydrogen cyanide react almost quantitatively in 8 days at the ordinary temperature; the product, on hydrolysis with aqueous potassium hydroxide, yields mesitylic acid.

[With ERICH LANGE.]—1 : 3-Dimethyl*cyclo*hexenone, dissolved in concentrated hydrochloric acid, was added to potassium cyanide and water cooled by ice and the mixture left for 5 days. The *additive* compound formed decomposes on distillation with evolution of hydrogen cyanide and formation of dimethyl*cyclo*hexenone ; when hydrolysed with aqueous potassium hydroxide, it yields 1 : 3-dimethyl*cyclo*hexanonecarboxylic acid. The *oxime*, $OH\cdot N\colon C_6H_7Me_2\cdot CO_2H$, forms white crystals and melts at 155—156° ; the *semicarbazone*, $C_{10}H_{17}O_3N_3$, is a microscopic, crystalline powder and melts at 203—205°. 1 : 3-Dimethyl*cyclo*hexane-5-ol-1 : 5-dicarboxylic acid, $C_{10}H_{16}O_5$, is formed by the action of hydrogen cyanide on dimethyl*cyclo*hexenone ; the reaction is accelerated by the addition of organic bases. G. Y.

Action of Magnesium Aryl Haloids on Dicarboxylic Acids. WALTHER DILTHEY and E. LAST (*Ber.*, 1904, 37, 3775).—Benzopinacone, and not β-benzopinacoline (this vol., i, 667), is the product of the action of magnesium phenyl bromide on ethyl oxalate. W. A. D.

Phenoquinone, Thiophenoquinone, and Quinhydrone. THEODOR POSNER (*Annalen*, 1904, 336, 85—167).—Thiophenoquinone (Tröger and Eggert, Abstr., 1896, i, 562) is best represented by the constitutional tautomeric formulæ, $CO<{CH(SPh)\cdot CH_2 \atop CH_2\cdot CH(SPh)}>CO$ and

$$OH\cdot C\lessdot{CH(SPh)\cdot CH \atop CH\cdot CH(SPh)}\gtrdot C\cdot OH,$$

which agree with its properties and with those of its derivatives. The formation of thiophenoquinone is explained on the basis of Thiele's theory of unsaturated compounds, the phenylmercaptan reacting with the conjugated system $O{:}\dot{C}\cdot CH{:}CH\cdot$ to form $OH\cdot\dot{C}{:}CH\cdot CH(SPh)\cdot$.

As thiophenoquinone resembles phenoquinone in its formation, colour, stability, and behaviour on acetylation or benzoylation, and in the formation of unstable blue alkali salts, the latter has probably the similar tautomeric constitution: $CO<{CH(OPh)\cdot CH_2 \atop CH_2\cdot CH(OPh)}>CO$ and

$$OH\cdot C\lessdot{CH(OPh)\cdot CH \atop CH\cdot CH(OPh)}\gtrdot C\cdot OH,$$

which agrees better with its properties than does the constitution suggested by Jackson and Oenslager (Abstr., 1895, i, 513).

Thiophenoquinone is formed by the action of phenyl mercaptan on a large excess of quinone in light petroleum; if the reaction takes place without a solvent, the mixture becomes black, develops heat, and yields a viscid, blue mass containing quinol and phenyl disulphide.

Thiophenoquinone is moderately stable in indifferent solvents such as benzene or light petroleum, but decomposes when dissolved in hydroxylic solvents such as alcohol or acetic acid; with cold dilute sodium hydroxide, it forms an unstable, dark blue sodium salt which rapidly becomes brown.

3 : 6-*Diphenylthiolquinone*, $CO<{C(SPh){:}CH \atop CH{:}C(SPh)}>CO$, is formed when a solution of thiophenoquinone, in carbon tetrachloride, is shaken with ice and aqueous potassium permanganate. It crystallises in orange-coloured, glistening leaflets, sinters at 252°, melts at 257°, and is insoluble in water, slightly soluble in alcohol or ether, but easily so in boiling glacial acetic acid. It is, in part, completely oxidised on prolonged shaking with an excess of potassium permanganate and sulphuric acid. When reduced with zinc dust in boiling glacial acetic acid solution, it yields 3 : 6-*diphenylthiolquinol*, which crystallises in colourless, rectangular plates, melts at 103°, and is easily oxidised to the 3 : 6-diphenylthiolquinone; the *diacetyl* derivative, $C_{22}H_{18}O_4S_2$, crystallises in colourless needles and melts at 168—168·5°.

When dissolved in light petroleum, thiophenoquinone gradually decomposes to thiophenol and quinone; the latter oxidises part of the unchanged thiophenoquinone to 3 : 6-diphenylthiolquinone, itself being reduced to quinol; at the same time, part of the thiopheno-

quinone, by loss and subsequent readdition of 1 mol. of thiophenol, and oxidation by the free quinone, yields 2 : 6-diphenylthiolquinone,

$$CO<\begin{matrix}C(SPh){:}CH\\C(SPh){:}CH\end{matrix}>CO.$$

The same reaction takes place, but more quickly, when thiophenoquinone is dissolved in alcohol, but with formation of an additional red substance.

2 : 6-Diphenylthiolquinone crystallises in cherry-coloured needles, melts at 203—204°, and is moderately soluble in boiling alcohol or glacial acetic acid. It is reduced by zinc dust and glacial acetic acid to a greasy *product* (2 : 6-diphenylthiolquinol ?) which, on oxidation with ferric chloride in aqueous alkaline solution, yields 2 : 6-diphenylthiolquinone, and with acetic anhydride forms the *diacetyl* derivative of 2 : 6-diphenylthiolquinol, which melts at 112—114°, and the diacetyl derivative of 3 : 6-diphenylthiolquinol.

The red *substance*, $C_{24}H_{14}O_4S_2$, which is obtained from the reaction of thiophenoquinone with alcohol, forms reddish-brown, glistening crystals, sinters at 85°, melts at 96°, and is easily reduced by zinc dust and acetic acid to a colourless *substance*; this, when boiled with acetic anhydride, yields the diacetyl derivative of 3 : 6-diphenylthiolquinol.

The action of thiophenol on 3 : 6- or 2 : 6-diphenylthiolquinone in boiling glacial acetic acid solution leads to the formation of 2 : 3 : 6-*triphenylthiolquinol*, which separates from alcohol in colourless crystals, melts at 111·5—112·5°, and yields a *diacetyl* derivative,

$$OAc\cdot C<\begin{matrix}C(SPh)\cdot C(SPh)\\C(SPh)\text{——}CH\end{matrix}>C\cdot OAc;$$

this forms hard, granular crystals and melts at 101—101·5°.

Oxidation of 2 : 3 : 6-triphenylthiolquinol in aqueous alkaline solution by the action of air or of ferric chloride leads to the formation of 2 : 3 : 6-*triphenylthiolquinone*, which crystallises in glistening, reddish-brown scales, melts at 169°, and is reduced to the quinol by zinc dust and glacial acetic acid. The action of hydroxylamine hydrochloride and sodium acetate on 3 : 6-diphenylthiolquinone in glacial acetic acid leads to the formation of 3 : 6-diphenylthiolquinol and of a *substance*, $C_{54}H_{42}O_6N_2S_6$, which crystallises in reddish-brown, glistening needles, melts at 235°, and has the constitution

$$OH\cdot C_6H_2(SPh)_2\cdot O\cdot CH<\begin{matrix}CH(SPh)\cdot C(N\cdot OH)\\C(N\cdot OH)\cdot CH(SPh)\end{matrix}>CH\cdot O\cdot C_6H_2(SPh)_2\cdot OH.$$

It yields a *tetra-acetyl* derivative which crystallises in brown needles and melts at 163°.

The oxidation of thiophenoquinone by potassium permanganate in presence of an excess of thiophenol leads to the formation of a *derivative* of 2 mols. of 2 : 3 : 6-diphenylthiolquinol and 1 mol. of 3 : 6-diphenylthiolquinol,

$$OH\cdot C_6H(SPh)_3\cdot O\cdot CH<\begin{matrix}C(SPh)\cdot C(OH)\\C(OH)\cdot C(SPh)\end{matrix}>CH\cdot O\cdot C_6H(SPh)_3\cdot OH,$$

which crystallises in brown leaflets, melts at 164°, and on reduction yields 2 : 3 : 6-triphenylthiolquinol and 3 : 6-diphenylthiolquinol.

[With J. Lipski].—When treated with benzyl mercaptan in light petroleum solution, quinone yields *dibenzylthioltetrahydroquinone*,

$$C_6H_6(SC_7H_7)_2O_2,$$

which crystallises in metallic, glistening needles, melts at 160—163°, and when boiled with acetic anhydride yields quinol. When oxidised by potassium permanganate in ice-cooled light petroleum solution, it yields *dibenzylthiolquinone*, $C_6H_2(SC_7H_7)_2O_2$, which crystallises in dark red leaflets, melts at 223—224°, and is reduced by zinc dust and glacial acetic acid to *dibenzylthiolquinol*, $C_6H_2(SC_7H_7)_2(OH)_2$. This crystallises from dilute alcohol, melts at 134—135°, and yields a *diacetyl* derivative which melts at 203—205°. When the solution of dibenzylthioltetrahydroquinone in light petroleum is exposed to light for some weeks, it is converted into dibenzylthiolquinone and a dark blue *substance*, which sinters at 120°, melts at 136°, and is oxidised by potassium permanganate to a red *powder*, $C_{26}H_{18}O_4S_2$, melting at 119—121°.

The action of benzyl mercaptan on dibenzylthiolquinone in boiling glacial acetic acid solution leads to the formation of *tribenzylthiolquinol*, $C_6H(SC_7H_7)_3(OH)_2$, which is colourless, melts at 94—98°, and yields dibenzylthiolquinone when oxidised with ferric chloride in alkaline solution, and the diacetyl derivative of dibenzylthiolquinol when boiled with acetic anhydride.

Amyl mercaptan and quinone form *diamylthioltetrahydroquinone*, which melts at 150—152° and is converted by alcohol or oxidation into *diamylthiolquinone*; this crystallises in red needles and melts at 170—172°. Reduction with zinc dust and acetic acid leads to the formation of *diamylthiolquinol*, which crystallises in colourless needles and melts at 68—70°; the *diacetyl* derivative forms white needles and melts at 103—106°.

Ethyl mercaptan and quinone form a small amount of an additive product; oxidation of the solution leads to *diethylthiolquinone*, which crystallises in red, feathery needles, melts at 159°, and is reduced by zinc dust and acetic acid to *diethylthiolquinol*. This crystallises in needles, melts at 49—50°, and forms a *diacetyl* derivative which melts at 133—134°.

2 : 5-Toluquinone and phenyl mercaptan in light petroleum form *diphenylthioltetrahydrotoluquinone* as a blue precipitate, which melts at 95—97° and after 24 hours has changed into toluquinol and phenyl disulphide.

Diphenylthioltoluquinone, formed by oxidation by potassium permanganate of a solution of toluquinone and thiophenol in petroleum, crystallises in red needles, melts at 141—142°, and is reduced by zinc dust and acetic acid to *diphenythioltoluquinol*, which sinters at 75° and melts at 78—80°; the *diacetyl* derivative crystallises in colourless needles and melts at 121—122°. Toluquinone and benzyl mercaptan, in light petroleum solution, form the *additive* product, $C_{14}H_{14}O_2S$ or $C_{21}H_{22}O_2S_3$, which melts at 101—103·5°, and on treatment with alcohol or oxidation with potassium permanganate yields *benzylthioltoluquinone*, $CO<\begin{matrix}CMe{=\!=}CH\\CH{:}C(SC_7H_7)\end{matrix}>CO$, which crystallises in red needles and melts at 136—137°. *Benzylthioltoluquinol* melts at 113—114·5° and yields a *diacetyl* derivative which crystallises in colourless needles and melts at 120—122°.

When warmed with benzyl mercaptan, benzylthioltoluquinone

forms *dibenzylthioltoluquinol*, $OH\cdot C\!\lessdot\!\begin{matrix}C(SC_7H_7)-CH\\CMe\!:\!C(SC_7H_7)\end{matrix}\!\gtrdot\!C\cdot OH$, which crystallises in long, colourless needles, sinters at 109°, and melts at 113°; the *diacetyl* derivative forms colourless needles and melts at 116—117°. The toluquinol is oxidised by ferric chloride to *dibenzylthioltoluquinone*, which is a brown, amorphous powder and melts at 67—68°.

Toluquinone reacts with ethyl and with amyl mercaptans in light petroleum solution to form small, dark precipitates which melt at about 102—103° and, on oxidation with potassium permanganate, yield oily products.

Xyloquinone and thiophenol do not react in a solvent, but when heated together at 100° yield xyloquinol and phenyl disulphide. Anthraquinone and phenanthraquinone do not react with thiophenol.

G. Y.

Introduction of Hydroxyl Groups into Anthraquinone and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 153129).—When anthraquinone is dissolved in concentrated sulphuric acid to which mercury or a mercuric salt has been added, and a current of nitrous acid is passed through the warmed solution, a vigorous reaction takes place and the mass becomes brown. The product consists chiefly of 1 : 4-dihydroxyanthraquinone (quinizarin). The same process may be applied to the derivatives of anthraquinone containing no hydroxyl; thus anthraquinone-2-sulphonic acid yields quinizarinsulphonic acid.

When phosphoric or arsenic acid, or phosphorus oxychloride, is also added to the solution, three hydroxyl groups are introduced, forming purpurin and its derivatives. The purpurinsulphonic acid prepared in this way is more stable than that obtained by direct sulphonation.

Sodium nitrite or nitrososulphuric acid may be employed instead of gaseous nitrous acid.

C. H. D.

Preparation of Hydroxy-derivatives of 1-Amino and 1-Alkylaminoanthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 154353).—When 1-aminoanthraquinone or its methyl or ethyl derivative is dissolved in fuming sulphuric acid (80 per cent.), oxidation takes place in the course of a few days to the corresponding 4-hydroxy-derivative.

C. H. D.

Condensation of Anthraquinone with Phenols. WASSILI SCHARWIN, NAUMOF, and SANDURIN (*Ber.*, 1904, **37**, 3616—3620. Compare Abstr., 1903, i, 640).—A better yield of phenolanthraquinone than that obtained from anthraquinone, phenol, and stannic chloride by the method previously described is obtained when the operation is conducted in an atmosphere of nitrogen.

Dichlorophenylanthraquinone chloride, $CCl_2\!\lessdot\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\gtrdot\!C(C_6H_4Cl)_2$, prepared by the action of phosphorus trichloride on diacetylphenolanthraquinone, separates in colourless prisms and melts at 158·5°. It forms a yellow solution with concentrated sulphuric acid.

Phenolanthraquinone dimethyl ether, $CO{<}{}^{C_6H_4}_{C_6H_4}{>}C(C_6H_4{\cdot}OMe)_2$, prepared by the Friedel-Crafts reaction from anthraquinone chloride and anisole, separates in yellow rhombohedra, melts at 208°, and forms a reddish-violet solution with concentrated sulphuric acid. Phenolanthraquinone was obtained as a product of its hydrolysis by aluminium chloride. When anthraquinone is condensed with dimethyl-*m*-aminophenol, pyronine is formed. *Pyronine hydrochloride* forms colourless needles and melts and decomposes at 223°. A. McK.

Bromine Derivatives of Phenanthraquinone. JULIUS SCHMIDT (*Ber.*, 1904, 37, 3551—3556).—A theoretical introduction to the following communications. G. Y.

The Phenanthrene Series. XI. Phenanthraquinone Dibromide. JULIUS SCHMIDT and ERHARD JUNGHAUS (*Ber.*, 1904, 37, 3556—3558).—The action of bromine on phenanthraquinone mixed with a small quantity of water and cooled by ice leads to the formation of *phenanthraquinone dibromide*, $C_{14}H_8O_2Br_2$, which is obtained as a reddish-brown mass. It rapidly decomposes with loss of bromine, and, when boiled with water, yields phenanthraquinone and 2-bromophenanthraquinone. G. Y.

The Phenanthrene Series. XII. 2-Bromophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ERHARD JUNGHAUS (*Ber.*, 1904, 37, 3558—3567).—*2-Bromophenanthraquinone*, $C_{14}H_7O_2Br$, prepared by heating phenanthraquinone with bromine in aqueous solution in a sealed tube at 100°, crystallises from glacial acetic acid in glistening, yellowish-red needles and leaflets, melts at 233—234°, dissolves in concentrated sulphuric acid to a green solution, which becomes reddish-brown when warmed, and, on further treatment with bromine, yields 2 : 7-dibromophenanthraquinone. 2-Bromophenanthraphenazine (bromodiphenylenequinoxaline), $C_6H_4{<}{}^{N:C\cdot C_6H_4}_{N:C\cdot C_6H_3Br}$, obtained when 2-bromophenanthraquinone is boiled with *o*-phenylenediamine hydrochloride in alcoholic solution, crystallises in sheaves of brown needles and melts at 252—254°. The *monoxime*,

$$C_{14}H_7OBr{:}NOH$$

(Abstr., 1902, i, 797), crystallises in orange-coloured, matted needles and melts at 163—164°. The *monophenylhydrazone*, $C_{14}H_7OBr{:}N_2HPh$, is formed by the action of phenylhydrazine hydrochloride on 2-bromophenanthraquinone in alcoholic solution; it crystallises in red needles and melts at 171—172°. The action of phenylhydrazine on 2-bromophenanthraquinone results in the reduction of the quinone to *2-bromo-8 : 9-dihydroxyphenanthrene*, which is unstable. The *diacetyl* derivative obtained by boiling the reduction product with acetic anhydride crystallises in sheaves of white needles and melts at 178—179°. The *monoimide*, $\begin{matrix} C_6H_3Br\cdot C{:}NH \\ | \qquad\quad | \\ C_6H_4 —— CO \end{matrix}$ (?), obtained by the action of alcoholic ammonia on 2-bromophenanthraquinone, crystallises in

glistening, golden needles, melts and decomposes at 169°, and dissolves in alcohol to a yellow solution which becomes green when boiled. The action of alcoholic ammonia on 2-bromophenanthraquinone at 130—140° leads to the formation of *dibromophenanthrazine*, $\begin{matrix} C_6H_3Br\cdot C\cdot N\cdot C\cdot C_6H_3Br \\ C_6H_4 — C\cdot N\cdot C\cdot C_6H_4 \end{matrix}$ or $\begin{matrix} C_6H_3Br\cdot C\cdot N\cdot C\cdot C_6H_4 \\ C_6H_4 — C\cdot N\cdot C\cdot C_6H_3Br \end{matrix}$, which crystallises in glistening, brown needles, does not melt at 350°, and sublimes without decomposition when strongly heated.

When heated at 100° with sulphuric acid containing 4 per cent. of sulphur trioxide, 2-bromophenanthraquinone yields a monosulphonic acid containing a small amount of disulphonic acid; with sulphuric acid containing 35 per cent. of sulphur trioxide at the ordinary temperature, it yields almost wholly the disulphonic acid.

2-*Bromophenanthraquinonesulphonic acid*, $C_{14}H_6O_2Br\cdot SO_3H$, forms a brownish-red, crystalline mass, is easily soluble in water, but insoluble in anhydrous organic solvents, forms *salts* which are easily soluble in water, and in aqueous solution colours wool-brown. 2-*Bromophenanthraquinonedisulphonic acid*, $C_{14}H_5O_2Br(SO_3H)_2$, resembles, but is more hygroscopic and darker coloured than, the monosulphonic acid. 2-Bromophenanthraquinone is oxidised by potassium dichromate and sulphuric acid to p-*bromodiphenic acid*, $C_6H_4(CO_2H)\cdot C_6H_3Br\cdot CO_2H$, which crystallises in white leaflets, melts at 238—239°, and forms a *silver* salt which crystallises in white needles. G. Y.

The Phenanthrene Series. XIII. 2 : 7-Dibromophenanthraquinone and its Derivatives. JULIUS SCHMIDT and ERHARD JUNGHAUS (*Ber.*, 1904, 37, 3567—3570).—2 : 7-*Dibromophenanthraquinone*, obtained by bromination of phenanthraquinone or of 2-bromophenanthraquinone at 150—160°, forms reddish-yellow needles and melts at 323°. It is also formed in small amount by the action of cuprous bromide on the diazo-solution obtained from 2 : 7-diaminophenanthraquinone (this vol., i, 70). 2 : 7-Dibromophenanthraquinone is oxidised by potassium dichromate and sulphuric acid to 4 : 4′-*dibromodiphenic acid*, which is also formed by the action of cuprous bromide on diazotised 4 : 4′-diaminophenic acid. It crystallises in white needles and melts at 277—278°.

2 : 7-Dibromophenanthraphenazine, $\begin{matrix} C_6H_3Br\cdot C:N \\ C_6H_3Br\cdot C:N \end{matrix} > C_6H_4$, crystallises in green needles and melts at 294—295°. 2 : 7-*Dibromophenanthraquinone monoxime*, $C_{14}H_7O_2Br_2N$, forms red needles and melts and decomposes at 229—230°. The *monoimide*, $C_{14}H_7Br_2ON$, crystallises in long, red needles and melts and decomposes at 231—232°. Tetrabromophenanthrazine, $C_{28}H_{12}N_2Br_4$, formed from 2 : 7-dibromophenanthraquinone, crystallises in microscopic needles and does not melt at 350°. G. Y.

The Phenanthrene Series. XIV. 3-Bromophenanthraquinone and its Derivatives. JULIUS SCHMIDT and GUSTAV LADNER (*Ber.*, 1904, 37, 3571—3572).—3-Bromophenanthraquinone,

obtained by oxidation of 3 : 9-(or 3 : 10-)dibromophenanthrene, crystallises in glistening, yellow needles, melts at 268°, and dissolves in cold concentrated sulphuric acid to a dark brown solution. It is oxidised by potassium dichromate and sulphuric acid to 5-*bromodiphenic acid*, which crystallises in white needles, melts and decomposes at 257°, and is converted by potassium permanganate in sulphuric acid solution into *p*-bromobenzoic acid.

3-*Bromophenanthraquinone monoxime* crystallises in slender, yellow needles and melts at 198°. 3-*Bromophenanthraphenazine* crystallises in yellow needles and melts at 249°. G. Y.

The Phenanthrene Series. XV. Bromo- and Bromonitro-derivatives of Phenanthrene. JULIUS SCHMIDT and GUSTAV LADNER (*Ber.*, 1904, **37**, 3573—3577).—9-Bromo-10-nitrophenanthrene, obtained by warming 9-bromophenanthrene with concentrated nitric acid (Werner, Abstr., 1902, i, 440), or better by the action of nitrogen peroxide on an ice-cold solution of 9-bromophenanthrene in benzene, is reduced by stannous chloride and hydrochloric acid in boiling glacial acetic acid solution to 10-aminophenanthrene (Abstr., 1903, i, 691).

When heated with bromine and water in a sealed tube at 100°, 10-nitrophenanthrene forms a *dibromide*, $C_{14}H_9O_2Br_2N$, which crystallises in glistening, yellow leaflets, melts at 81—82°, and is not oxidised when warmed with chromic acid in glacial acetic acid solution.

The action of bromine on phenanthrene in boiling chloroform solution leads to the formation of 3 : 9-(or 3 : 10-)dibromophenanthrene (see foregoing abstract), which melts at 146° (Werner, *loc. cit.*).

G. Y.

Preparation of Solid Camphene. CHEMISCHE FABRIK AUF AKTIEN VORM E. SCHERING (D.R.-P. 154107. Compare this vol., i, 680).—Solid camphene, free from chlorine, is obtained on heating, under pressure, pinene hydrochloride, hydrobromide, or hydriodide with aqueous solutions of piperidine, or of the fatty bases, such as methylamine, dimethylamine, diamylamine, or piperazine. C. H. D.

Terpenes and Ethereal Oils. LXIX. Phellandrene. OTTO WALLACH [with ERICH BESCHKE] (*Annalen*, 1904, **336**, 9—46. Compare Abstr., 1887, 967; 1888, 1204; 1891, 1084; 1896, i, 101; 1901, i, 89; 1903, i, 105).—*d*-Phellandrene, obtained from elemi oil, is chemically and physically identical with *d*-phellandrene from bitter-fennel oil, but not with *d*-phellandrene from water-fennel oil. The former is to be called *d*-α-, the latter *d*-β-phellandrene. *l*-Phellandrene, from eucalyptus oil, is *l*-α-phellandrene. *d*-α-Phellandrene is now found to boil at 61° under 11 mm. pressure and to have a sp. gr. 0·844 at 19°, and n_D 1·4732.

The two nitrites formed from α-phellandrene (Schreiner, Abstr., 1901, i, 600) are separated by recrystallisation from acetone and alcohol. *d*-α-Phellandrene α-nitrite melts at 112—113° and has $[\alpha]_D - 138·4°$; *l*-α-phellandrene α-nitrite melts at 112—113° and has $[\alpha]_D + 135·93°$ to $+ 142·6°$. *d*-α-Phellandrene β-nitrite melts at 105° and has $[\alpha]_D + 45·8°$; *l*-α-phellandrene β-nitrite melts at 105° and has

$[\alpha]_D$ $-40{\cdot}287°$ to $-40{\cdot}817°$. The α- and β-nitrites of α-phellandrene are chemically identical. Contrary to Semmler's statement (Abstr., 1903, i, 641), they are only slowly oxidised by potassium permanganate in acetone solution. When acted on by nitric acid in glacial acetic acid solution, they yield *trinitro-*p*-cymene*, $C_{10}H_{15}O_6N_3$, which crystallises in yellow prisms, melts at 136—137° (Abstr., 1901, i, 89), and has $[\alpha]_D$ $+191{\cdot}0°$ to $+195{\cdot}92°$ when prepared from the nitrites of *l*-α-phellandrene, $-188{\cdot}13°$ to $-188{\cdot}30°$ when prepared from the nitrites of *d*-α-phellandrene. When reduced with zinc and hydrochloric acid, it yields 2 : 5-diamino-*p*-cymene dihydrochloride. When warmed with fuming hydrochloric acid at 60°, α-phellandrene nitrite yields *p*-cymene, a small amount of a *ketone*, which boils above 200° under the ordinary pressure, dichlorothymoquinone (Andreson, *J. pr. Chem.*, 1881, [ii], 23, 176), which melts at 99°, and chlorothymoquinone (Kehrmann, Abstr., 1900, i, 180), which forms a *semicarbazone*, $C_{11}H_{14}O_2N_3Cl$, melting at 230°. When warmed with tin and hydrochloric acid until the yellow colour disappears, dichlorothymoquinone yields *chlorothymoquinol*, $C_{10}H_{13}O_2Cl$, which melts at 70°; if the heating with tin and hydrochloric acid is prolonged, the product is thymoquinol.

The action of sulphuric acid (3 of acid : 2 of water) on α-phellandrene nitrite leads to the formation of (1) *p*-cymene; (2) a *ketone* which boils at 110—114° under 16 mm. pressure and forms an *oxime*, $C_{10}H_{17}ON$(?), melting at 87—88°; (3) *hydroxythymoquinone*, $C_{10}H_{12}O_3$, which forms red crystals, melts at 170°, boils at 125—134° under 16 mm. pressure, and yields a *semicarbazone*, $C_{11}H_{15}O_3N_3$, melting at 214—217°, and (4) thymoquinone.

Nitro-α-phellandrene, obtained from α-phellandrene nitrite, is isomeric with Pesci's nitrophellandrene (Abstr., 1896, i, 101), which was formed from β-phellandrene nitrite, and has $[\alpha]_D$ approximately the same as for the nitrite from which it is obtained. When reduced with zinc dust in acetic acid solution, nitro-α-phellandrene yields *l*-carvotanacetone ($\Delta^{5,6}$-methene-2-one), its oxime, and a small amount of a base (dihydrocarvacrylamine?). *l*-Carvotanacetone boils at 227—229°, has an intense odour of carvone, a sp. gr. 0·9345, n_D 1·4822 at 19°, and, with hydrogen sulphide in alcoholic ammoniacal solutions, forms an additive compound which crystallises in needles and melts at 220°. The oxime, $C_{10}H_{16}\colon NOH$, crystallises in prisms and melts at 75—76°; the oxime derived from *l*-α-phellandrene has $[\alpha]_D$ $-19{\cdot}155°$, that from *d*-α-phellandrene has $[\alpha]_D$ $+19{\cdot}20°$; on crystallisation of a molecular mixture of the lævo- and dextro-rotatory oximes, the racemic modification melting at 92—93° is obtained. The semicarbazone crystallises in needles which change into transparent prisms, melts at 173°, and has $[\alpha]_D$ $-112{\cdot}40°$ to $-113{\cdot}79°$ if obtained from *l*-α-phellandrene, $[\alpha]_D$ $+114{\cdot}69°$ if from *d*-α-phellandrene; the racemic modification obtained by crystallising a molecular mixture of the dextro- and lævo-rotatory modifications melts at 177—178° (compare Semmler, Abstr., 1900, i, 676; Harries, Abstr., 1901, i, 551).

From the constitution of carvotanacetone are to be derived the constitutional formulæ for nitro-α-phellandrene,

$$CMe{<}\begin{matrix}C(NO_2)\colon CH\\CH\text{—}CH_2\end{matrix}{>}CHPr^{\beta},$$

for α-phellandrene nitrite, $CMe{<}{}^{CH(NO_2)\cdot CH(NO)}_{CH\text{———————}CH_2}{>}CHPr^{\beta}$, and for α-phellandrene, $CMe{<}{}^{CH{=}CH}_{CH\cdot CH_2}{>}CHPr^{\beta}$.

d-β-Phellandrene boils at 57° under 11 mm. pressure and has a sp. gr. 0·8520, n_D 1·4788 at 20°, and $[\alpha]_D$ +18·54°. The nitrite melts at 98° (see Abstr., 1903, i, 105) and on recrystallisation from acetone yields an α-modification, which melts at 102° and has $[\alpha]_D$ −159·3°, and a β-modification, which melts at 97—98° and in 8·5 per cent. solution shows no optical activity.

When reduced with zinc dust and acetic acid, nitro-β-phellandrene yields chiefly a diamine (Abstr., 1903, i, 105) and a small amount of a *ketone* which boils at 111—112° under 13 mm. pressure, and has a characteristic odour resembling neither carvone nor menthone; the *semicarbazone* crystallises in white needles, becomes yellow on exposure to light, and melts at 200—202°; the *oxime* melts at 42—44° and boils at 150° under 12 mm. pressure. G. Y.

Matico Oil and Matico-camphor. HERMANN THOMS (*Chem. Centr.*, 1904, ii, 1125; from *Apoth.-Zeit.*, 19, 771—773).—The composition of a sample of matico oil obtained by Schimmel & Co. from leaves of *Piper angustifolium*, received in April, 1904, has been found to be quite different from that examined previously. It contained 10 per cent. of asarone, together with cineol, a mixture of terpenes, and a hydrocarbon, but, unlike the earlier sample, neither dill-apiole nor parsley-apiole. Matico-camphor, $C_{15}H_{26}O$, melts at 94° and has $[\alpha]_D$ −28·73°. The camphor is a sesquiterpene alcohol, since on boiling with a 50 per cent. solution of sulphuric acid it forms a sesquiterpene with elimination of water. E. W. W.

Oleum Pini Sylvestris and Oleum Pini Strobi. JULIUS TRÖGER and ALFRED BEUTIN (*Arch. Pharm.*, 1904, **242**, 521—532). —Two samples of oil were examined, obtained from young twigs gathered in the spring. One was obtained from *Pinus sylvestris*, grown in Germany, and had a sp. gr. 0·871 at 20°; it contained 3·23 per cent. of esters (reckoned as bornyl acetate) and 9·3 per cent. of alcohols (reckoned as bornyl alcohol). *d*-Pinene was present in quantity, but neither sylvestrene nor cadinene could be detected, although these are present in needles gathered in the winter (Bertram and Walbaum, Abstr., 1893, i, 660).

The second sample was purchased in Germany, but was called "Weymouth pine oil"; it had sp. gr. 0·901 at 15°, n_D 1·4827 at 20°, and α_D −39·70° in a 200 mm. tube, and it contained 8·6 per cent. of esters and 5·2 per cent. of alcohols (calculation as before). *l*-Pinene was present in quantity, but no other substance could be isolated with certainty. C. F. B.

Copaiva Balsam from Surinam. LEOPOLD VAN ITALLIE and C. H. NIEUWLAND (*Arch. Pharm.*, 1904, **242**, 539—546).—Some samples were examined which had been collected in Surinam from *Copaifera guianensis*, and found by J. F. Pool to contain 78 per cent.

of essential oil when fresh; the acid number was 34, the iodine number 94; esters were not present. The *essential oil* was obtained by distillation with water, had a sp. gr. 0·91 and boiled between 250° and 260°; from a solution of the residual resin in alcohol, a crystalline *copaivic acid* melting at 130° had been isolated. The bulk of the oil boiled at 254—262° and seemed to be a mixture of two *sesquiterpenes*. From the fraction boiling at 270—280°, a little cadinene dihydrochloride was prepared by diluting the fraction with ether and passing hydrogen chloride in. Towards the end of the distillation of the balsam with steam, a crystalline *sesquiterpene alcohol*, $C_{15}H_{26}O$ (molecular weight determined), melting at 113—115°, separated in the condenser; this gave the reactions of a cholesterol, but seemed not to form an acetate when warmed with acetic anhydride in pyridine solution. C. F. B.

Constituents of White Peru Balsam. HERMANN THOMS and A. BILTZ (*Chem. Centr.*, 1904, ii, 1047; from *Zeit. Oesterr. Apoth.-V.*, 42, 943—947. Compare Abstr., 1902, i, 634).—The following substances have been isolated from white Peru balsam: (1) myroxocerin (compare Germann, Abstr., 1897, ii, 185), a white, amorphous substance, which melts at 120—130°, and is soluble in benzene, ethyl acetate, or chloroform, but insoluble in absolute alcohol or alkalis. (2) A compound which crystallises from dilute alcohol in needles, melts and decomposes at 270°, and is soluble in a 5 per cent. solution of sodium carbonate. This substance does not contain nitrogen. (3) Cinnamic acid. (4) A brownish-yellow substance which may be extracted by means of a 1 per cent. solution of potassium hydroxide and softens at 100° (myroxol). By the action of an alcoholic solution of potassium hydroxide on the balsam, cinnamic acid, cinnamyl alcohol, and phenylpropyl alcohol are formed. The balsam probably also contains a hydrocarbon which has the odour of cedar wood. The presence of benzyl alcohol and peruviol was not detected. E. W. W.

Galbanic Acid. ALEXANDER TSCHIRCH and K. G. v. KÜYLENSTJERNA (*Arch. Pharm.*, 1904, 242, 533—537).—A sample of this acid sent by Hirschsohn (compare Tschirch and Knitl, Abstr., 1899, i, 714) has been examined. It melts at 155—156° and has the composition $C_{13}H_{20}O_2$. If this is the molecular formula (molecular weight determinations gave uncertain results), the acid is monobasic; the *silver* and *barium* salts were analysed; the acid number is about 11 per cent. less than the theoretical, and the saponification number is little greater; the iodine number is about 8 per cent. less than corresponds with the presence of one ethylene linking; an acetyl derivative could not be prepared. C. F. B.

Caoutchouc. Latex from Sicily. CARL D. HARRIES (*Ber.*, 1904, 37, 3842—3848. Compare Weber, Abstr., 1903, i, 845; de Jong and de Haas, this vol., ii, 762, 763).—The fresh juice of *Ficus magnoloöides* has been examined. When extracted with ether and the ethereal solution filtered and evaporated, an oil is obtained consisting of a mix-

ture of an oxygen compound, $C_{30}H_{48}O_3$, and an elastic substance of the same composition as paracaoutchouc (Abstr., 1902, i, 811). It also yields the same nitrosite. The oxygen compound begins to crystallise when the oil is kept, but the two compounds are most readily separated by solution in ether and precipitation with alcohol, in which the elastic mass is insoluble. Its solubility in ether also diminishes as the oxygen compound is removed. It also becomes less soluble after repeated treatment with formic acid.

The oxygen compound crystallises from alcohol in colourless plates, melts at 115° after sintering at 111°, and occurs in large quantity in the extract. *Ficus elastica* yields an oxygen compound, $C_{20}H_{32}O_2$, which sinters at 185° and melts at 195°. This is mixed with about an equal quantity of the elastic substance in the original extract.

J. J. S.

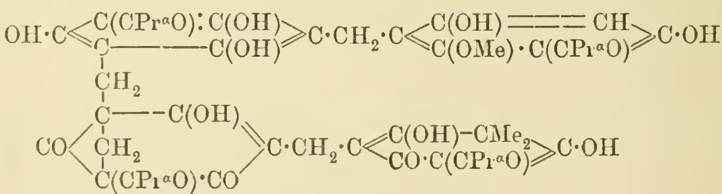
Caper-rutin. D. H. Brauns (*Arch. Pharm.*, 1904, 242, 556—560. Compare this vol., i, 681).—Caper-rutin was isolated from caper buds that had been preserved in vinegar, by extraction with boiling water; from dried buds that had already opened, no rutin could be obtained. Caper-rutin is identical in properties and reactions with the rutin of rue (Waliaschko, this vol., i, 760) and with sophorin (following abstract); each of these substances yields rhamnose and dextrose on hydrolysis with dilute sulphuric acid, in addition to a product, $C_{15}H_{10}O_7$ (quercetin, sophoretin), which in all three cases exhibits the same properties and reactions. C. F. B.

Sophorin. D. H. Brauns (*Arch. Pharm.*, 1904, 242, 547—556. Compare this vol., i, 681).—Sophorin, $C_{27}H_{30}O_{16}$, was extracted from Chinese yellow-berries by boiling the drug, which consisted of flower buds, flower stalks, and stems, with water, and allowing the extract to cool, when the glucoside crystallised out; the yield of the crude substance was 27 per cent. When dried in the air, it contains nearly $3H_2O$; when dried over sulphuric acid, under diminished pressure, it retains $2H_2O$, and then takes up the additional H_2O when exposed to the air; it does not do this after it has been dried at 110°, when it loses all its water. The sophoretin, $C_{15}H_{10}O_7$, obtained by hydrolysing sophorin with dilute sulphuric acid, melts at 297—300°, and crystallises with $2H_2O$, which are lost at 100°, and slowly at the ordinary temperature under diminished pressure; in the latter case, they are taken up again in the air, not so when the drying has been effected at 100°. In these respects, and also in respect of its acetyl derivative, sophoretin is identical with quercetin. Rhamnose and dextrose were also identified as products of the hydrolysis of sophorin, which takes place in accordance with the equation $C_{27}H_{30}O_{16} + 3H_2O = C_{15}H_{10}O_7 + C_6H_{14}O_6 + C_6H_{12}O_6$; evidently sophorin is identical with rutin from rue (Waliaschko, this vol., i, 760. C. F. B.

Filmarone, the Anthelmintic Substance in Filix Extract. Friedrich Kraft (*Arch. Pharm.*, 1904, 242, 489—500. Compare Abstr., 1902, i, 814, and Boehm, Abstr., 1898, i, 40; 1899, i, 32, 804; 1902, i, 36, &c.; this vol., i, 403, 406, &c.).—The substance

previously described by the author as flavaspidin is probably identical with Boehm's phloraspin (this vol., i, 409).

The amorphous acid previously described, which forms the chief component of the extract, is now named *filmarone*. When heated for 8 hours with zinc dust and 15 per cent. aqueous sodium hydroxide, it yields filicic acid, a substance melting at 137°, filicyl-*n*-butanone (Boehm, Abstr., 1902, i, 36), methylphloroglucinyl methyl ether, melting at 118—119°, phloroglucinol, and trimethylphloroglucinol, with some methyl- and dimethyl-phloroglucinols and butyric acid. If the boiling is continued for 5 minutes only, merely traces of filicic acid are obtained and more of the substance melting at 137°. This was identified with aspidinol or methylphloroglucinylbutanone methyl ether (Boehm, Abstr., 1902, i, 37). After repeated recrystallisation, it melted at 155—158°. With diazoaminobenzene in alcoholic solution, filmarone yields benzenedisazophloroglucinyl-*n*-butanone (Boehm, Abstr., 1902, i, 39); in carbon tetrachloride solution, benzeneazomethylphloroglucinyl-*n*-butanone (*ibid.*, 38) is obtained. In consequence of these decompositions, the formula given below, equal to $C_{47}H_{54}O_{16}$, is assigned to filmarone; it is supported by the ascertained percentages of carbon and hydrogen, of methoxyl and of butyric acid, and by the percentage of calcium in the *calcium* salt (filmarone functions as a dibasic acid).



Filmarone.

C. F. B.

Theory of Dyeing. Richard Willstätter (*Ber.*, 1904, 37, 3758—3760).—If, in dyeing, the dye combines chemically with the fibre, it might be possible by such a process to resolve a racemic substance which is absorbed by the fibre into its antipodes. Experiments were made from this standpoint with the inactive alkaloids atropine, homatropine, and tropacocaine, which are absorbed from their solutions in considerable quantity by wool; in all cases, however, both the alkaloid absorbed by the wool and that left behind in solution were equally inactive.

W. A. D.

Transformation of True Colour Bases into Carbinol Bases and of True Cyanide Dyes into Leuco-cyanides. Paul Gerlinger (*Ber.*, 1904, 37, 3958—3963).—The transformation of a true colour base into the corresponding carbinol and of a true cyanide dye into a leuco-cyanide is a reaction of the second order. The following transformations were studied: brilliant-green base at 0°, crystal-violet base at 0° and at 25°, pararosaniline base at 0° and at 25°, pararosaniline cyanide at 25°, and auramine base at 25°.

A. McK.

Melanic Pigments. MARUSSIA BAKUNIN and G. DRAGOTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 222—240).—The pigment investigated by the author was isolated from melanotic nodules by means of sodium carbonate solution, which converted it into a soluble compound, probably the sodium salt. The pigment was then re-precipitated by hydrochloric acid.

The material thus obtained consists of a mixture of at least two different substances: (1) dull brown melanin, which does not give concordant numbers on analysis, and (2) shining black *melanin*, to which the formula $C_{39}H_{58}O_{15}N_6S$ is given. The latter yields with aqueous ammonia a *hydroxide* of the formula $C_{39}H_{56}O_{15}N_6S(OH)_2$, and also forms a *silver* salt, $C_{39}H_{56}O_{15}N_6SAg_2$.

The brown, dull melanin, when treated with an alcoholic solution of piperidine and the liquid precipitated with hydrochloric acid, yields a black *pigment*, $C_{60}H_{89}O_{18}N_6S$, which is slightly soluble in acetic acid and readily in ammonia or sodium hydroxide solution; it gives a *silver* salt, $C_{60}H_{84}O_{18}N_6SAg_5$. T. H. P.

Chlorocoumalinic Acid and its Conversion into Pyridine Derivatives. HANS VON PECHMANN and WILLIAM H. MILLS (*Ber.*, 1904, 37, 3829—3836. Compare Feist, Abstr., 1901, i, 557).—The *chlorocoumalinic acid* obtained by the action of chlorine in an acetic acid solution of coumalinic acid in the presence of iodine has the constitution $CO_2H\cdot C{<}{\substack{CH:CCl\\CH\text{—}O}}{>}CO$, since it can be converted into 3-chloropyridine. It forms compact crystals from acetic acid, melts at 187—189°, and is sparingly soluble in chloroform or benzene. It dissolves in sodium carbonate solution and can be precipitated unaltered on the addition of acid; both sodium hydroxide and boiling water decompose it.

The *methyl* ester, obtained by esterifying the acid, or even better by chlorinating methyl coumalinate, crystallises in colourless, thick prisms and melts at 134—136°. It is decomposed when boiled with water, is insoluble in sodium carbonate solution, but dissolves in the corresponding hydroxide. Concentrated ammonia converts the methyl ester into *methyl 3-chloro-2-hydroxypyridine-5-carboxylate*,

$$CO_2Me\cdot C{<}{\substack{CH:CCl\\CH\text{—}N}}{\gg}C\cdot OH,$$

which crystallises from water in prismatic needles melting at 218°. It possesses acidic properties, and crystalline *sodium* and *barium* derivatives have been prepared. The free *acid* crystallises in plates, melts and decomposes at 308°, and is only sparingly soluble in the usual organic solvents. The majority of its salts are sparingly soluble.

2 : 3-*Dichloropyridine-5-carboxylic acid*, obtained by the action of phosphorus oxy- and penta-chlorides on the hydroxy-acid, crystallises from dilute alcohol with $1H_2O$, melts at 162—163°, and yields a characteristic *lead* salt which forms feathery crystals. When the acid is heated, it loses hydrogen chloride and yields a product from which chloropyridonecarboxylic acid has been obtained.

The dichloro-acid, on reduction with hydriodic acid, potassium iodide, and red phosphorus, yields 3-*chloropyridine-5-carboxylic acid*, which melts at

170—171° and is very sparingly soluble in benzene. Its silver salt, when heated, yields chloronicotinic acid and 3-chloropyridine, which is extremely stable towards sodic methoxide (compare Lieben and Haitinger, Abstr., 1885, 966). J. J. S.

Action of Hydrazine Hydrate on Methyl Bromocoumalinate. HANS VON PECHMANN and WILLIAM H. MILLS (*Ber.*, 1904, 37, 3836—3841).—*Methyl 3-bromo-1-amino-2-pyridone-5-carboxylate*,

$$NH_2\cdot N<\begin{matrix}CO\text{———}CBr\\CH{:}C(CO_2Me)\end{matrix}>CH,$$

is obtained by the action of a 50 per cent. solution of hydrazine hydrate on methyl bromocoumalinate. It may be separated from unaltered coumalinate by solution in hydrochloric acid, crystallises from benzene or hot water, and melts at 144—145·5°. It is only feebly basic, and solutions of its salts precipitate the base on the addition of much water. It readily condenses with benzaldehyde, yielding a *hydrazone*, $C_7H_5O_3Br\cdot N\cdot N{:}CHPh$, which crystallises in minute, colourless needles melting at 173°, and on treatment with nitrous acid yields methyl bromohydroxynicotinate and nitrous oxide.

3-*Bromo*-1-*amino*-2-*pyridone*-5-*carboxylic acid*, obtained by hydrolysing the ester with methyl alcoholic sodium hydroxide, melts at 238° and its aqueous solution has a sweet taste and reduces Fehling's solution on boiling. It condenses with benzaldehyde, yielding *benzylideneaminobromopyridonecarboxylic acid*, $C_{13}H_9O_3N_2Br$, which melts at 243°. The methyl ester reacts with methyl bromocoumalinate yielding *methyl* 3 : 3'-*dibromo*-1 : 1'-*dipyridonyl*-5 : 5'-*dicarboxylate*,

$$CH<\begin{matrix}C(CO_2Me){:}CH\\CBr\text{———}CO\end{matrix}>N\cdot N<\begin{matrix}CH{:}C(CO_2Me)\\CO\text{———}CBr\end{matrix}>CH,$$

which crystallises from nitrobenzene in small prisms melting at 344°, and is sparingly soluble in all ordinary solvents. On reduction, it yields methyl bromopyridonecarboxylic acid. J. J. S.

An Organic Persulphate. ROBERT FOSSE and P. BERTRAND (*Compt. rend.*, 1904, 139, 600—602. Compare this vol., i, 816).—*Dinaphthaxanthonium sulphate*, $CH<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O\cdot O\cdot SO_2\cdot OH$, obtained by the action of dilute sulphuric acid on dinaphthaxanthydrol or on bisdinaphthaxanthen oxide, forms red crystals containing 1 mol. of sulphuric acid and varying proportions of water according to the strength of the acid employed in the preparation; it reacts with potassium iodide to form dinaphthaxanthen tri-iodide (di-iododinaphthaxanthonium iodide? Compare Abstr., 1902, i, 304, 689) and bisdinaphthaxanthen, according to the equation:

$$3CH<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O\cdot O\cdot SO_2\cdot OH + 3KI =$$
$$3KHSO_4 + CH<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O,I_3 + \left(CH<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O\right)_2,$$

and with alcohol to form aldehyde and dinaphthaxanthen,

$$CH_2<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>O$$

(*loc. cit.*), and is therefore to be regarded as a derivative of Caro's monopersulphuric acid, $H \cdot O \cdot O \cdot SO_2 \cdot OH$. M. A. W.

Pyrone. RICHARD WILLSTÄTTER and RUDOLF PUMMERER (*Ber.*, 1904, 37, 3740—3752).—Chelidonic acid gives, with an aqueous solution of sodium chloride, a very sparingly soluble, characteristic, hyperacid *salt*, $C_7H_4O_6,C_7H_3O_6Na$. Pyrone is best prepared by distilling dry chelidonic acid with copper powder, which serves to equalise the temperature; like dimethylpyrone, it readily forms additive compounds with acids and with metallic salts.

The *hydrochloride*, $C_5H_4O_2,HCl$, precipitated on adding pyrone to hydrogen chloride in ether, melts at 139°, crystallises from alcohol, and is hygroscopic. Two oxalates of pyrone exist: the one, $C_5H_4O_2,C_2H_2O_4$, is obtained in ethereal solution, crystallises from water in leaflets, and melts at 136·5°; the *other*, $3C_5H_4O_2,C_2H_2O_4$, is formed in aqueous solution, crystallises in thick, transparent prisms, and melts at 139°. Two crystalline *aurichlorides*, $3C_5H_4O_2,HAuCl_4$ and $2C_5H_4O_2,HAuCl_4$, may also be obtained; both melt at 116·5°. The *picrate*, $C_{11}H_7O_9N_3$, crystallises from water or alcohol and melts at 129°. With calcium chloride in alcoholic solution, pyrone combines to form the crystalline additive *compound*, $2C_5H_4O_2,CaCl_2$, which deliquesces in the air. *Pyrone mercurichloride*, $C_5H_4O_2,HgCl_2$, crystallises in thin plates and melts at about 170°. *Pyrone silver nitrate*, $4C_5H_4O_2,7AgNO_3$, melts and decomposes at 162°.

Pyrone does not combine with alkali hydroxides, but is decomposed by them. With potassium methoxide, however, in methyl alcohol, a colourless, crystalline *compound*, $C_5H_4O_2,CH_3 \cdot OK$, is obtained; the sodium methoxide *derivative*, $C_5H_4O_2,C_2H_5 \cdot ONa$, is formed similarly. With benzoyl chloride, pyrone potassium methoxide in ethereal suspension interacts to form a *methylbenzoate*, $C_{13}H_{12}O_4$, which crystallises from ether or alcohol in plates and melts at 98·5—99°. It is probable that the alkyloxide derivatives have the formula $O<\genfrac{}{}{0pt}{}{CH:CH}{CH:CH}>C(OMe) \cdot OK$, and the methylbenzoate the structure $O<\genfrac{}{}{0pt}{}{CH:CH}{CH:CH}>C(OMe) \cdot OBz$. It is thus the carbonyl group which reacts additively in these cases, whilst in the simple salts formed with acids the oxygen of the same group is perhaps quadrivalent; the hydrochloride, for instance, has probably the structure

$$O<\genfrac{}{}{0pt}{}{CH:CH}{CH:CH}>C:O:HCl.$$

Ethyl chelidonate combines additively with sodium ethoxide, but the product, unlike those obtained from pyrone, is soluble in ether, and therefore probably is formed by addition to the carbethoxyl radicle. With a large excess of mercuric chloride, the ester gives the *compound* $2C_{11}H_{12}O_6,HgCl_2$; with less mercuric chloride, the *compound* $4C_{11}H_{12}O_6,3HgCl_2$, is obtained; both substances are crystalline. *Methyl chelidonate*, $C_9H_8O_6$, melts at 122·5°. *Chelidonamide*, $C_5H_2O_2(CO \cdot NH_2)_2$, formed instantaneously by the action of ammonia on ethyl chelidonate dissolved in alcohol, crystallises from water in microscopic, infusible needles. W. A. D.

Isomeric Coninium Iodides. MAX SCHOLTZ (*Ber.*, 1904, 37, 3627—3638).—By the interaction of *N*-ethylconiine and benzyl iodide, a mixture of two isomeric *benzylethylconinium iodides* is formed, which can be separated by means of chloroform. The *a-iodide* is sparingly soluble in chloroform and crystallises from water in colourless needles, melting at 178° and having $[\alpha]_D + 21.2°$ at 20° in methyl alcohol; the *β-iodide* obtained on evaporating the chloroform mother liquors melts at 208° and has $[\alpha]_D + 31.2°$ at 20°. The *platinichloride* of the *a-chloride* crystallises in prisms melting at 195°; the *platinichloride* of the *β-chloride*, which is sparingly soluble in water, from which it crystallises in rhombic prisms, blackens at 215° and melts at 218°. N-*Benzylconiine,* prepared by the action of benzylchloride and an alkali hydroxide on coniine, boils at 294—296° (corr.), has a sp. gr. 0·9461 at 20°/4°, and $[\alpha]_D$ 72·9° at 20°; it reacts only very slowly with ethyl iodide. At temperature of the water-bath, the isomeric iodides are formed; at 120°, an interchange in position of the ethyl and benzyl groups takes place, resulting in the formation of ethylconiine hydroiodide.

In a similar manner, *iso*amylconiine and benzyl iodide react, forming isomeric *benzylisoamylconinium iodides*: the *a-iodide* crystallises from water in prisms melting at 169° and has $[\alpha]_D$ 26·6° at 20°; the *β-iodide* crystallises from acetone in needles, melts at 185°, and has $[\alpha]_D + 33.3°$ at 20°. The *a-chloride* forms a *platinichloride* sparingly soluble in hot water, from which it crystallises in rhombohedra melting at 188°; the *β*-iodide gives this salt, as well as a second, more soluble *platinichloride,* melting at 199°. The *a*-iodide forms a *picrate,* crystallising in prisms with pyramidal ends, melting at 129°, and this compound is also obtained from the *β*-iodide. *Benzylmethylconinium iodide* exists as an *a*-iodide melting at 187° and a *β*-form melting at 215°, only a relatively small proportion of the *β*-compound being formed.

Methyl benzylconiniumacetate iodide, $CH_2Ph\cdot C_9H_{16}NI\cdot CH_2\cdot CO_2Me$, prepared from methyl coniine-*N*-acetate and benzyl iodide, also exists in two forms; the *a*-iodide melts at 103°, whilst the *β*-form crystallised from acetone melts at 146°. *Methylconiine*-N-*acetate* is a colourless liquid boiling at 244—245°, and having a sp. gr. 0·9726 at 20°/4° and $[\alpha]_D + 62.1°$ at 20°. *Dibenzylconinium iodide* crystallises in prisms melting at 176°, and exists in one form only. E. F. A.

Certain Salts of Quinine. HENRI CARETTE (*J. Pharm. Chim.*, 1904, [vi], 20, 347—355).—When crystallised from water, normal quinine hydrochloride contains $2\frac{1}{2}H_2O$. This salt is hygroscopic, begins to melt at 80°, becomes brown at 215°, and above that temperature forms a black liquid. The water of crystallisation is lost at 102°, no hydrogen chloride being evolved, giving a yellow, anhydrous salt, which becomes colourless on cooling. When crystallised from alcohol, either absolute or 30 per cent., the salt contains 1·5 mols. alcohol, which is lost either at 100°, when some hydrogen chloride is given off, or in a vacuum. Too long heating or exposure to light renders the dry salt yellow. At 35—50° the salt loses its alcohol and yields by absorption of moisture the hydrochloride with $\frac{1}{2}H_2O$, which is more stable and

less hygroscopic than the anhydrous compound. The latter salt becomes yellow at 165—170°, forming a brown liquid at 180—185°, and has $[\alpha]_D - 233°$.

Crystallographic measurements of the salt containing alcohol of crystallisation are given in the paper. G. D. L.

Papaverinium Bases. HERMAN DECKER (*Ber.*, 1904, 37, 3809—3815. Compare this vol., i, 338).—[With OSKAR KLAUSER.]—*Papaverine butyl bromide*, obtained by heating the components for 12 hours at 100°, is solid, melts at 109°, and then resolidifies and melts and decomposes on further heating at 217°. With alkalis, it yields the yellow *butyl*iso*papaverine*, which is not readily obtained in a crystalline form. With dilute hydrochloric acid, it yields *papaverinium butyl chloride*, $C_{24}H_{30}O_4NCl,2H_2O$, melting at 131—132°. The *picrate* melts at 151—152°, the *mercurichloride* melts and decomposes at 200°, and the *platinichloride* at 204°.

Papaverine iso*butyl iodide* crystallises from alcohol in yellow, glistening prisms melting at 171—172°. *Papaverine* p-*nitrobenzyl chloride* melts and decomposes at 131°, the *mercurichloride* melts at 188°, the *picrate* at 183—184°. On treatment with alkali, the chloride does not yield a yellow *iso*-base, but is completely decomposed, turning black and evolving ammonia. *Papaverine* iso*propyl iodide* melts at 93—94°.

[With M. GIRARD.]—Bromopapaverine has been prepared by a modification of Anderson and Goldschmidt's method (*Monatsh.*, 1885, 6, 674). Its *hydrochloride* melts sharply at 197°, the *picrate* melts and decomposes at 125°. The bromine is not removed by treatment with alkali at 200°. The brominated base yields a *methiodide* crystallising in yellow cubes and melting and decomposing at 225°. The base also combines directly with methyl sulphate without any solvent, and the aqueous solution of the product on treatment with alkali yields N-*methyl brom*iso*papaverine*,

$$C_6H_2Br(OMe)_2\cdot CH{:}C{<}\begin{matrix}NMe\text{---}CH\\C_6H_4(OMe_2)\end{matrix}{>}CH,$$

which forms yellow crystals melting at 122° and is much more stable than the *iso*-bases previously obtained. It combines but slowly with water, and is only slowly oxidised by atmospheric oxygen.

Bromopapaverine benzyl chloride, on treatment with alkali, yields N-*benzylbromo*iso*papaverine*, which crystallises in yellow needles melting at 113°. It is stable, and on oxidation with permanganate yields 6-bromoveratric acid (Koelle, *Ber.*, 1878, 136) and 6 : 7-dimethoxy-2-benzyl-1-*iso*quinolone (this vol., i, 339).

When less permanganate is used, 6-*bromoveratraldehyde* melting at 150° is obtained. The bromo-acid melts at 186°. J. J. S.

Products of the Addition of Alkyl Haloids to Sparteine. MAX SCHOLTZ and P. PAWLICKI (*Arch. Pharm.*, 1904, 242, 513—520). —An attempt was made to find whether the two nitrogen atoms in the diacid tertiary base sparteine have a similar function, by adding 1 mol. each of two different alkyl iodides in succession, the order of succession being varied, and noting whether the final products in the two cases were isomeric or identical; they were found to be isomeric. Sparteine monomethiodide (Bamberger, Abstr., 1887, 163), melting at

234°, unites with ethyl iodide to form a *compound* melting at 239°, whereas the *compound* formed from the monoethiodide (which melts at 231°) and methyl iodide melts at 246°, and a mixture of the two compounds has an ill-defined melting point at about 15° lower. *Sparteine monobenzyliodide* melts at 230°, the *compound* of this with methyl iodoacetate at 219°; the additive *product* from the alkaloid and 1 mol. of methyliodoacetate melts at 230°, the *compound* of this with benzyl iodide at 245°. The *compound* of the monomethiodide with methyl iodoacetate melts at 232°, the *compound* from the methyl iodoacetate additive product and methyl iodide at 249°.

The compound $C_{15}H_{26}N_2$,MeI,HI, however, obtained by the action of methyl iodide on sparteine hydriodide, is identical, not isomeric, with that obtained from sparteine and methyl iodide in methyl alcoholic solution at 100°, in which circumstances the monomethiodide is first formed, for it is the final product in the cold.

When the compound $C_{15}H_{26}N_2$,MeI,HI is decomposed with concentrated aqueous potassium hydroxide, sparteine monomethiodide is precipitated, identical with that obtained from sparteine and methyl iodide in the absence of alcohol; no sparteine is precipitated, contrary to Bamberger's statement.

With *iso*amyl iodide, sparteine yields *compounds* containing 1 or 2 mols. of the iodide according to the proportions employed; these melt at 229° and 230° respectively. In the presence of alcohol, the compound $C_{15}H_{26}N_2,C_5H_{11}I$,HI, melting at 227°, is formed. With *o*-xylylene bromide in chloroform solution, the compound

$$C_{15}H_{26}N_2,C_6H_4(CH_2Br)_2,$$

melting at 237°, is formed. C. F. B.

Action of Pyrocinchonic Anhydride on the Phenylenediamines. Luciano Rossi (*Real. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 122—132).—The author has prepared *o*-phenylenepyrocinchonic diamide and *m*- and *p*-aminophenylenepyrocinchonimides by the action, either alone or in alcoholic solution, of molecular proportions of pyrocinchonic anhydride and the particular phenylenediamine. These compounds are all soluble in alcohol, acetone, benzene, or chloroform.

o-*Phenylenepyrocinchonic diamide*, $C_6H_4<\begin{matrix}NH\cdot CO\cdot CMe\\ \| \\ NH\cdot CO\cdot CMe\end{matrix}$, crystallises from alcohol in yellow prisms melting at 150—154°.

m-*Aminophenylenepyrocinchonimide*, $NH_2\cdot C_6H_4\cdot N<\begin{matrix}CO\cdot CMe\\ \| \\ CO\cdot CMe\end{matrix}$, forms greenish-yellow crystals melting at 160°.

p-*Aminophenylenepyrocinchonimide*, $NH_2\cdot C_6H_4\cdot N<\begin{matrix}CO\cdot CMe\\ \| \\ CO\cdot CMe\end{matrix}$, crystallises in golden-yellow needles melting at 140°.

By using two mols. of pyrocinchonic anhydride to one of the phenylenediamine, the following di-acid imides were obtained:

*Phenylene-*o*-dipyrocinchonimide*, $C_6H_4\left(N<\begin{matrix}CO\cdot CMe\\ \| \\ CO\cdot CMe\end{matrix}\right)_2$, crystallises in tufts of white needles melting at 139—140°.

Phenylene-m-*dipyrocinchonimide*, $C_{18}H_{16}O_4N_2$, crystallises from alcohol in tufts of faintly cream-coloured needles melting at 175°.

Phenylene-p-*dipyrocinchonimide*, $C_{18}H_{16}O_4N_2$, crystallises in pale cream needles or, from acetone, in hexagonal prisms, which begin to turn brown at 200° and melt at 285°.

m-*Phenylenephthalylpyrocinchonimide*,

$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot C_6H_4\cdot N{<}{}^{CO\cdot CMe}_{CO\cdot CMe},$$

crystallises from alcohol or acetone in white needles and from benzene in small prisms, which melt at 212° and are soluble in chloroform.

p-*Phenylenephthalylpyrocinchonimide*, $C_{20}H_{14}O_4N_2$, crystallises from benzene in white needles, which begin to turn brown at above 200° and melt at 274—275°; it is soluble in chloroform and to a slight extent in alcohol or acetone. T. H. P.

Action of Pyruvic and Pyrotartaric Acids on the *p*-Aminophenols. G. Giuffrida and A. Chimienti (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iii], 10, 109—121).—p-*Hydroxyphenylpyrotartrimide*, $\begin{matrix}CHMe\cdot CO\\ CH_2\text{---}CO\end{matrix}{>}N\cdot C_6H_4\cdot OH$, prepared by the action of either pyruvic or pyrotartaric acid on *p*-aminophenol, separates from water or alcohol in crystals melting at 230°.

p-*Methoxyphenylpyrotartrodiamide*,

$$OMe\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot CHMe\cdot CO\cdot NH\cdot C_6H_4\cdot OMe,$$

obtained by the action of either pyruvic or pyrotartaric acid on *p*-anisidine, crystallises from alcohol in pearly white needles melting at 241—242°. When heated in a sealed tube with concentrated hydrochloric acid at 110°, it yields pyrotartaric acid, *p*-aminophenol hydrochloride, and methyl chloride. The *dinitro*-derivative, $C_{19}H_{20}O_4N_2(NO_2)_2$, is deposited from acetic acid solution in minute, yellow crystals melting at 202°, and the *dibromo*-compound, $C_{19}H_{20}O_4N_2Br_2$, crystallises in small, yellow needles melting at 82—83°.

p-*Methoxyphenylpyrotartrimide*, $\begin{matrix}CHMe\cdot CO\\ CH_2\text{---}CO\end{matrix}{>}N\cdot C_6H_4\cdot OMe$, the principal product of the interaction of pyrotartaric acid and *p*-anisidine, crystallises from alcohol in white prisms melting at 95°; it has the normal molecular weight in freezing benzene.

p-*Methoxyphenylpyrotartramic acid*,

$$CO_2H\cdot CH_2\cdot CHMe\cdot CO\cdot NH\cdot C_6H_4\cdot OMe,$$

obtained by the action of alcoholic potassium hydroxide on *p*-methoxyphenylpyrotartrimide, forms crystals melting at 137°.

p-*Ethoxyphenylpyrotartrodiamide*,

$$OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot CHMe\cdot CO\cdot NH\cdot C_6H_4\cdot OEt,$$

prepared by the interaction of pyruvic or pyrotartaric acid and *p*-phenetidine, crystallises from alcohol in long, white needles melting at 234—235° and soluble in acetic acid. When heated in a sealed tube with concentrated hydrochloric acid, it yields pyrotartaric acid, *p*-aminophenol hydrochloride, and ethyl chloride. The *nitro*-derivative, $C_{21}H_{25}O_4N_2\cdot NO_2$, separates from acetic acid in minute crystals, melt-

ing at 195°; the *bromo*-compound, $C_{21}H_{25}O_4N_2Br$, crystallises from alcohol in milk-white, silky needles, melts at 74°, and is extremely soluble in alcohol.

p-*Ethoxyphenylpyrotartrimide*, $C_3H_6<\substack{CO\\CO}>N\cdot C_6H_4\cdot OEt$, obtained by the action of pyrotartaric acid on *p*-phenetidine, is deposited from alcohol in crystals melting at 97°.

p-*Methoxyphenyliminopyruvic acid*, $CO_2H\cdot CMe\vdots N\cdot C_6H_4\cdot OMe$, prepared by the action of pyruvic acid on *p*-anisidine in alcoholic solution, is obtained as an amorphous, yellow product which is insoluble in the ordinary solvents and decomposes, giving pyrotartrodiamide, on heating.

p-*Ethoxyphenyliminopyruvic acid*, $CO_2H\cdot CMe\vdots N\cdot C_6H_4\cdot OEt$, prepared from pyruvic acid and *p*-phenetidine, is a yellow, amorphous substance, which begins to melt at 105° and is completely fused at about 228°.

T. H. P.

Preparation of Pure *iso*Stilbazoline. ALBERT LADENBERG (*Ber.*, 1904, 37, 3688—3692. Compare Abstr., 1903, i, 275, and this vol., i, 92).—*d*- and *l*-Stilbazolines have been obtained by the aid of the acid tartrates, namely, *d*-stilbazoline hydrogen *l*-tartrate and *l*-stilbazoline hydrogen *d*-tartrate. The values of $[\alpha]_D$ for the free bases at 18° are respectively $+12\cdot16°$ and $-11\cdot5°$. The sp. gr. is 0·9699.

When the two bases are mixed, no rise in temperature occurs and hence no true racemic compound is formed.

To obtain *iso*stilbazoline, the acid *d*-tartrates are first prepared, the *l*- and *iso*-bases are precipitated as salts, and the *d*-base remains in solution. The mixed *d*- and *iso*-bases are then converted into normal *l*-tartrates, when the iso*stilbazoline* l-*tartrate* crystallises out, even when the solution is fairly strongly acid (1—3 mols. of base to 1 mol. of acid). This salt forms colourless, hexagonal plates and melts at 214—215°. The *base* has $[\alpha]_D$ $-5\cdot82°$, a sp. gr. 0·9727 at 19°, and it distils at 162° under 26 mm. pressure. The base may also be isolated in the form of its *d*-camphorsulphonate.

The normal *l*-tartrate of *l*-stilbazoline crystallises also in six-sided plates, melts at 211—212°, and contains $\frac{1}{2}H_2O$. It is not readily precipitated in acid solution, and thus differs from the corresponding salt of the *iso*-base.

One hundred parts of water at 17° dissolve 12·96 parts of the salt of *l*-base or 12·05 parts of the salt of the *iso*-base.

The *hydrochlorides* of the two bases are similar; they crystallise from acetone in colourless needles or prisms; that of the *l*-base melts at 149—150° and that of the *iso*-base at 150—151°. The *aurichlorides* are also similar, and melt at 116—117° and 117—118° respectively.

J. J. S.

[Coloured Quinoline Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 154448).—Alcoholic potassium hydroxide converts the alkyl iodides and chlorides of quinoline, and such of its derivatives as contain no methyl group in the pyridine ring, into dyes, which are not identical with the cyanines. In each case, a red and a

yellow dye are obtained, both of which may be used in the preparation of orthochromatic photographic plates. The appearance and solubility of a number of these derivatives is described. C. H. D.

Mechanism and Limits of the Phthalone Reaction. ALEXANDER EIBNER (*Ber.*, 1904, 37, 3605—3612).—The methyl group in quinaldine reacts with phthalic anhydride to form the compound $C_9NH_6 \cdot CH_2 \cdot C(OH) \lt {C_6H_4 \atop O} \gt CO$, where one of the two carbonyl groups in phthalic anhydride reacts, and also quinolylacetophenonecarboxylic acid, $CO_2H \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot C_9NH_6$ (compare Eibner and Lange, Abstr., 1901, i, 348). In the production of quinophthalone, the former product is first formed, from which an asymmetric quinophthalone (quinophthalide) results; then follows the formation of quinolylacetophenonecarboxylic acid, which afterwards yields a symmetric quinophthalone. The first three of these stages occur between 100° and 155°; the final stage is complete at about 210°.

Quinaldine condenses with benzaldehyde much more readily than does lepidine. A similar variance in the behaviour of quinaldine and lepidine is shown by the behaviour with phthalic anhydride. Whilst the former yields quinophthalone, the latter, when heated with a molecular amount of phthalic anhydride at 240° for 3 hours, forms a tarry mass, which gives no phthalone reaction. The question is discussed as to which ring compounds besides quinaldine are capable of yielding phthalones.

Naphthalic anhydride condenses with quinaldine to form *quinonaphthalone*, which forms yellow needles and melts at 256°.

A. McK.

Derivatives of 2-Amino-5-ethoxyphenol. FERDINAND HENRICH and F. SCHIERENBERG (*J. pr. Chem.*, 1904, [ii], 70, 325—331. See this vol., i, 1006).—2-Amino-5-ethoxyphenol, obtained by reduction of α-nitrosoresorcinol ethyl ether (Kietaibl, Abstr., 1899, i, 344), yields 4-aminoresorcinol when heated with concentrated hydrochloric acid in a sealed tube at 150°. The action of benzoyl chloride on 2-amino-5-ethoxyphenol in 10 per cent. sodium hydroxide solution leads to the formation of a *monobenzoyl* derivative which melts at 187° and, when distilled, yields 5-*ethoxy*-1-*phenylbenzoxazole*, $OEt \cdot C_6H_3 \lt {N \atop O} \gt C \cdot C_6H_5$, which is also formed when the hydrochloride of 2-amino-5-ethoxyphenol is heated with benzoyl chloride. It forms glistening, broad crystals, melts at 64—66°, and dissolves easily in organic solvents and in concentrated sulphuric acid to fluorescent solutions. The *diacetyl* derivative of 2-amino-5-ethoxyphenol, formed when the hydrochloride is heated with acetic anhydride, crystallises in thick prisms and melts at 91—93°. Along with the diacetyl compound, there is formed a small quantity of a *substance* which melts at 132°.

When oxidised by a current of air passed through its solution in aqueous sodium hydroxide, 2-amino-5-ethoxyphenol yields the

phenoxazine derivative, $OEt\cdot C_6H_3<^{N}_{O}>C_6H_2O\cdot NH_2$, which forms red crystals, melts at 280°, dissolves in sulphuric acid to a violet solution which becomes red on dilution, and yields an *acetyl* derivative, $C_{16}H_{14}O_4N_2$, which crystallises from a mixture of glacial acetic acid and acetic anhydride. The *hydrochloride*, $C_{14}H_{12}O_3N_2,HCl$, is dark violet and is hydrolysed by boiling, more slowly by cold water.

G. Y.

Quinonoidal Derivatives of Benzidine. I. RICHARD WILLSTÄTTER and LUDWIG KALB (*Ber.*, 1904, **37**, 3761—3775).—Dimethylaniline is instantaneously oxidised by potassium permanganate in presence of dilute sulphuric acid, giving diphenoquinonetetramethyldi-imonium disulphate (*infra*), which, by reduction with sulphurous acid, is easily converted into tetramethylbenzidine, $C_{12}H_8(NMe_2)_2$; the latter substance is easily prepared in this way and melts at 193·5° (Michler gives 195°, Ullmann, this vol., i, 269, gives 197°).

The green substance formed by the oxidation of tetramethylbenzidine with ferric chloride (Lauth, Abstr., 1891, 457) has the probable composition $C_{16}H_{21}ON_2Cl,2H_2O$, rather than that assigned to it by Lauth; its purification is difficult, as it is comparatively unstable. It probably has the constitution

$$NMe_2Cl\colon C_6H_4\colon C<^{CH\colon CH}_{CH\colon CH}>C(OH)\cdot NMe_2,$$

of a quinoneimonium salt containing an imino-ψ-quinol radicle. The green salt is converted by an excess of hydrochloric acid into an orange-coloured salt, which, however, is stable only in presence of this excess and cannot be isolated. But the corresponding sulphate, *diphenoquinonetetramethyldi-imonium disulphate*,

$$SO_4H\cdot NMe_2\colon C_6H_4\colon C_6H_4\colon NMe_2\cdot SO_4H,2H_2O,$$

is obtained by passing an excess of chlorine through a solution of tetramethylbenzidine in alcoholic sulphuric acid; it crystallises in red prisms, decomposes gradually in moist air, and dissolves in water giving an intensely orange-coloured solution.

Diphenoquinonetetramethyldi-imoniumplatinichloride,

$$C_{16}H_{20}N_2Cl_6Pt,2H_2O,$$

is obtained by dissolving the foregoing green salt in hydrochloric acid, which turns it into the orange dichloride, and adding platinic chloride; it forms slender, dark violet-coloured needles and is more stable than the other salts. On mixing the green chloride dissolved in hydrochloric acid with potassium iodide, a reddish-brown *periodide*,

$$NMe_2I\colon C_6H_4\colon C_6H_4\colon NMe_2I\cdot I_2,$$

is obtained; with an excess of water containing hydrochloric acid, this salt suddenly changes into a black, crystalline *salt*,

$$NMe_2\cdot C(OH)<^{CH\colon CH}_{CH\colon CH}>C\colon C_6H_4\colon NMe_2I,I_2,$$

belonging to the same series as the green chloride already described.

The green diphenoquinonetetramethyldi-imonium chloride is converted by an excess of gaseous sulphur dioxide, or by a solution of sodium sulphate to which acid is added, into *tetramethylbenzidine sulphonic acid*, $C_{16}H_{20}O_3N_2S$; this crystallises from dilute acetic acid in

colourless, six-sided leaflets, from alcohol in small rhombohedra or in needles, melts and decomposes at 261·5°, and gives crystalline *sodium*, *potassium*, and *ammonium* salts. The same acid may be obtained by directly sulphonating tetramethylbenzidine.

s-Dimethylbenzidine is prepared by the following method. Benzidine is converted by means of toluene-*p*-sulphonic chloride into ditoluene-*p*-sulphonebenzidine, $C_{12}H_8(NH \cdot SO_2 \cdot C_7H_7)_2$, which crystallises from acetone, on diluting, in large leaflets and melts at 243°; this substance is methylated in alkaline acetone solution by means of methyl sulphate, the product, *di-*p*-toluenesulphonedimethylbenzidine*,

$$C_{12}H_8(NMe \cdot SO_2 \cdot C_7H_7)_2,$$

crystallising from glacial acetic acid in aggregates of leaflets and melting at 235°. *Dimethylbenzidine*, $C_{12}H_8(NHMe)_2$, obtained by its decomposition with dilute sulphuric acid, crystallises from dilute alcohol, melts at 74—76°, and gives a crystalline *hydrochloride* melting at 149°. The green oxidation *product* of dimethylbenzidine obtained by the addition of ferric chloride has the composition $C_{14}H_{17}ON_2Cl$, and is converted by hydrochloric acid and platinic chloride into *diphenoquinonedimethyldi-imonium platinichloride*, $C_{14}H_{16}N_2Cl_6Pt,H_2O$, which forms golden-brown prisms. W. A. D.

A New Application of the Pyridine Method of Acylation. KARL AUWERS (*Ber.*, 1904, **37**, 3899—3903. Compare this vol., i, 736, and Dieckmann, this vol., i, 845, 873).—In the treatment of hydroxyl compounds containing a basic group with acyl chlorides, the acylation commences as a general rule in the basic group, the hydroxyl only being attacked subsequently. The direct preparation of *O*-acyl derivatives has therefore only been possible in such cases when the basic group has been protected by neighbouring groups, as in *o*-hydroxybenzyl-*o*-nitroaniline. It is now found that the preparation of *O*-acyl derivatives may be effected by the pyridine method, provided that the compound has acid properties and that the basic properties of the second constituent are not too pronounced. When these conditions are not fulfilled, either the *N*-derivatives or the mixed *ON*-diacyl derivatives are obtained.

A large excess of acyl chloride is usually required, and the *O*-derivatives obtained remain unchanged when treated with an excess of acyl chloride in pyridine solution, whereas *N*-derivatives are readily converted under the same conditions into diacyl derivatives. The reaction is in some cases complicated by the occurrence of secondary reactions due to the presence of the pyridine (compare succeeding abstracts). C. H. D.

Transformation of *O*-Acyl Compounds into *N*-Derivatives. KARL AUWERS (*Ber.*, 1904, **37**, 3903—3905).—It has been shown (this vol., i, 736) that phenol esters undergo a transformation into *N*-derivatives when a group NHR occupies the ortho-position with respect to the phenolic hydroxyl, or the α-position in an ortho-side-chain, R being hydrogen, or an alkyl or aryl group. The transformation usually occurs so rapidly that it is not possible to isolate the *O*-derivative. It is

now found (compare succeeding abstracts) that the *O*-acetates of *O*-hydroxyaldehyde phenylhydrazones are stable, but are converted into *N*-derivatives by boiling with either glacial acetic acid or pyridine. The reaction cannot be explained by the occurrence of hydrolysis, but must be regarded as an intramolecular rearrangement which is accelerated by those reagents. C. H. D.

Observations on Acylation. KARL AUWERS and R. BONDY [and, in part, K. MÜLLER] (*Ber.*, 1904, **37**, 3905—3915).—The *N*-acetate of tribromo-*p*-hydroxy-*m*-xylylene dianilide,

$$OH\cdot C_6Br_3(CH_2\cdot NHPh)\cdot CH_2\cdot NPhAc,$$

was found by Auwers and Hampe (Abstr., 1900, i, 96) to yield only a diacetate on further acetylation, although there should be in this case no steric hindrance. It is now found that a triacetate may be prepared by heating with acetic anhydride and sodium acetate, although the purification of the product is difficult. The *triacetate*,

$$OAc\cdot C_6H_3(CH_2\cdot NPhAc)_2,$$

crystallises slowly from light petroleum containing a little benzene in flat, glistening needles and melts at 145°. It separates from alcohol or ether in snow-white needles containing solvent of crystallisation.

Dilute sulphuric acid removes 1 mol. of acetic acid, as may be determined by titration, but only a charred product remains. Fusion at 200° with potassium hydroxide hydrolyses the triacetate to the NN-*diacetate*, $OH\cdot C_6H_3(CH_2\cdot NPhAc)_2$, crystallising from alcohol in long, flat tablets, melting at 207—208°, and dissolving moderately in benzene, alcohol, or acetic acid, sparingly in ether or light petroleum. The isomeric ON-*diacetate*, obtained by adding acetyl chloride to the monoacetate dissolved in pyridine, and extracting the product with alcohol to remove triacetate, crystallises from alcohol in small, well-formed leaflets, melts at 200—201°, and dissolves readily in benzene or chloroform, moderately in acetic acid or ethyl acetate, sparingly in alcohol.

The N-*acetate* of *tribromo*-p-*hydroxy*-m-*xylylene di*-p-*toluidide*,

$$OH\cdot C_6Br_3(CH_2\cdot NH\cdot C_6H_4Me)\cdot CH_2\cdot NAc\cdot C_6H_4Me,$$

prepared from *p*-toluidine and pentabromo-*m*-xylenol acetate, crystallises from toluene in groups of slender, white needles melting at 206°, and dissolves readily in acetone, acetic acid, ethyl acetate, or chloroform, less readily in alcohol or benzene. The *triacetate* crystallises from light petroleum-benzene in pearly prisms melting at 154° and yielding an NN-*diacetate* on hydrolysis, which, however, was only obtained in an amorphous form. The ON-*diacetate*, obtained by acetylating the monoacetate in pyridine solution, forms pearly leaflets and melts at 187—188°.

The N-*acetate* of the corresponding *o*-toluidide crystallises from benzene in thick, glistening prisms melting at 190—191°; the ON-*diacetate* separates from alcohol in leaflets and melts at 193°.

The compounds described by Biltz and Grimm (Abstr., 1899, i, 502) as monoacetates of the phenylhydrazones of the two *m*-nitrosalicylaldehydes are found to be *ON*-diacetates.

It was not found possible to acetylate 5-nitro-3-methylsalicylaldehyde, although the two isomeric compounds, in which the hydroxyl is

also situated between two ortho-groups, readily yield triacetates (compare following abstract). C. H. D.

Phenylhydrazones of Aromatic Hydroxyaldehydes. I. KARL AUWERS and R. BONDY (*Ber.*, 1904, 37, 3915—3929. Compare preceding abstracts).—The hydroxyaldehydephenylhydrazones investigated yield *N*-acetates with acetic anhydride and *ON*-diacetates on further acetylation. With acetyl chloride in pyridine solution, on the other hand, they yield almost exclusively *O*-acetates. The *O*-acetates of ortho-compounds may undergo a rearrangement to *N*-acetates, while the para-derivatives are stable.

5-*Nitro*-2-*hydroxy*-3-*methylbenzaldehyde*, prepared by nitrating *o*-homosalicylaldehyde, crystallises from light petroleum in slender, white needles, melting at 134° and becoming yellow after a time, or from glacial acetic acid in pale yellow scales. The *phenylhydrazone*, $C_{14}H_{13}O_3N_3$, crystallises from acetic acid, alcohol, or benzene in yellow, highly refractive needles melting at 206—207°. Moist ether converts it into red crystals of a *compound*, $C_{14}H_{15}O_4N_3$, which is probably a hydrate. Heat, or crystallisation from solvents, converts the red modification into the yellow. The N-*acetate* forms long, white, silky needles and melts at 241—242°. Sodium hydroxide does not dissolve the crystalline compound, but when precipitated by water from alcoholic solution it dissolves readily and may be reprecipitated by carbon dioxide. The *N*-acetate may also be prepared synthetically from the nitroaldehyde and α-acetylphenylhydrazine, $NPhAc{\cdot}NH_2$.

The O-*acetate*, obtained by acetylation in pyridine solution, exists in two modifications, one of which forms red plates or broad needles and melts at 205—206°, while the second forms yellow crystals, passing into the red modification at 175° and dissolving more readily in alcohol or benzene than the red crystals. The nature of the isomerism has not been determined.

Warming with pyridine or glacial acetic acid partially converts the *O*-acetate into the *N*-acetate.

The ON-*diacetate* crystallises from alcohol in slender, white needles and melts at 199—200°.

The *phenylhydrazone* of 3-*nitro*-2-*hydroxy*-5-*methylbenzaldehyde*, $C_{14}H_{13}O_3N_3$, crystallises from alcohol in yellow plates and melts at 164—166°. The N-*acetate* forms thick, yellow crystals melting at 252—253°, previously softening, and dissolves readily in sodium hydroxide, sparingly in organic solvents. It may also be prepared synthetically by means of α-acetylphenylhydrazine. The O-*acetate* crystallises from acidified alcohol in silky, yellow, felted needles melting at 155—156°. The ON-*diacetate* forms yellow needles, melting slowly at 130—150° and possibly consisting of a mixture of isomerides.

3-*Nitro*-2-*hydroxy*-5-*methylbenzaldehyde triacetate*,

$$NO_2{\cdot}C_6H_2Me(OAc){\cdot}CH(OAc)_2,$$

crystallises from a mixture of benzene and light petroleum in rosettes of thick, white needles melting at 132—132·5°.

3-*Nitro*-4-*hydroxy*-5-*methylbenzaldehydephenylhydrazone* crystallises from acetic acid in orange, hexagonal plates melting at 153—155°.

The N-*acetate* forms glistening, golden needles and melts at 188—189°. The O-*acetate* forms flat, orange needles and leaflets melting at 162—163°. It was not found possible to convert the O-acetate into the *N*-derivative.

3-*Nitro-4-hydroxy-5-methylbenzaldehyde triacetate* forms colourless plates melting at 117—118°. C. H. D.

Phenylhydrazones of Aromatic Hydroxyaldehydes. II. KARL AUWERS and O. BÜRGER (*Ber.*, 1904, 37, 3929—3937. Compare preceding abstract).—5-*Nitrosalicylaldehydephenylhydrazone* O-*acetate*, prepared by acetylation in pyridine solution, separates from alcohol in ruby-red needles or from chloroform in orange, silky leaflets. A small quantity of the N-*acetate* is produced at the same time, and may also be prepared by heating the *O*-acetate with acetic acid. It crystallises from ethyl acetate in slender, white needles and melts at 165°. The *ON*-diacetate was prepared by Biltz and Grimm (Abstr., 1899, i, 502), but erroneously described by them as a monoacetate.

5-*Nitrosalicylaldehyde triacetate*, $NO_2 \cdot C_6H_3(OAc)CH(OAc)_2$, forms colourless, rhombic prisms melting at 114—115°.

6-Nitrosalicylaldehydephenylhydrazone *ON*-diacetate is identical with Biltz and Grimm's monoacetate.

3-*Nitro-4-hydroxybenzaldehydephenylhydrazone* O-*acetate* forms orange needles melting at 134—135°. The N-*acetate* forms golden needles melting at 193—194°; the ON-*diacetate* forms yellow needles.

5-*Bromosalicylaldehydephenylhydrazone* forms flat, yellow needles melting at 151°. The O-*acetate* forms glassy, yellow needles melting at 138°; the N-*acetate* forms long, white, felted needles melting at 152°; the ON-*diacetate* forms flat, white needles and melts at 136—137°.

5-*Bromo-3-nitrosalicylaldehyde*, obtained by the nitration of bromosalicylaldehyde, crystallises from benzene-light petroleum in yellow needles melting at 147—148°. The *phenylhydrazone* forms large, dark brown needles melting at 243°. It yields an O-*acetate*, crystallising in red needles and melting at 209—210°; an N-*acetate*, forming colourless needles melting at 248°; and an ON-*diacetate* forming pale yellow needles melting at 203—204°. C. H. D.

Acylation of Compounds with Mixed Functions. KARL AUWERS and K. SONNENSTUHL (*Ber.*, 1904, 37, 3937—3943).—Benzoylation of salicylaldehydephenylhydrazone in pyridine solution yields only the O-*benzoate*, crystallising from alcohol in colourless tablets melting at 148—149°. Boiling with aniline or pyridine does not cause rearrangement to an *N*-derivative, but partially regenerates the hydrazone, forming the ON-*dibenzoate*, which crystallises in colourless needles and melts at 170—171°.

p-Hydroxybenzaldehydephenylhydrazone also yields an O-*benzoate*, crystallising in bundles of glistening needles and melting at 166—167°.

Dibromo-*p*-hydroxy-ψ-cumylaniline, $OH \cdot C_6Br_2Me_2 \cdot CH_2 \cdot NHPh$, yields an O-*benzoate* melting at 174—175°. The N-*benzoate*, prepared by Claisen's method, melts at 163—165°.

Dibromo-*o*-hydroxybenzylaniline, on the other hand, yields on benzoylation in pyridine solution the N-*benzoate*, melting at 167—168°, in consequence of the intramolecular rearrangement undergone by ortho-derivatives (compare this vol., i, 736).

p-Aminophenol yields the *ON*-dibenzoate, together with some *N*-benzoate melting at 213°.

m-Aminobenzyl alcohol yields only the ON-*dibenzoate* melting at 113—114°. Alcoholic sodium hydroxide converts it into the N-*benzoate* melting at 115°.

Hydroxyethylaniline yields the *ON*-dibenzoate. Diphenylhydroxyethylamine, $OH \cdot CHPh \cdot CHPh \cdot NH_2$, yields only the *N*-benzoate (Söderbaum, Abstr., 1896, i, 483). *iso*Diphenylhydroxyethylamine N-*benzoate*, prepared by partial hydrolysis of the dibenzoate, melts at 223°.

C. H. D.

Mutual Replacement of Hydrazine Residues in Hydrazones and Osazones. EMIL VOTOČEK and R. VONDRÁČEK (*Ber.*, 1904, 37, 3848—3854. Compare Ofner, this vol., i, 936).—Two isomeric mixed osazones may be obtained by the action of phenylmethylhydrazine acetate on dextrosephenylhydrazone or on lævulosephenylhydrazone. The one (A) melting at 192° is regarded as $\alpha\beta$-diphenyl-β-methylglucosazone, and the one melting at 205° (B) as $\alpha\beta$-diphenyl-α-methylglucosazone. The formation of these isomerides indicates that the hydrazine groups are only loosely combined in the hydrazone, and this has been confirmed by the replacement of one hydrazine residue by another in various phenylhydrazones and osazones. As a rule, the replacement does not occur with alcoholic solutions, but readily in the presence of acetic acid. Benzaldehydephenylmethylhydrazone is readily transformed into the corresponding phenylhydrazone, and this, in its turn, can be converted back into the phenylmethylhydrazone. An aqueous solution of galactosephenylhydrazone with phenylmethylhydrazine acetate at the ordinary temperature yields the phenylmethylhydrazone. Arabinosephenylmethylhydrazone can be obtained in a similar manner. Dextrosephenylhydrazone can be transformed into the β-naphthylhydrazone in alcoholic solution at the ordinary temperature without the aid of acetic acid. Galactosephenylbenzylhydrazone under similar conditions yields the phenylmethylhydrazone.

Phenylmethylhydrazine does not appear to react with galactose-*p*-bromophenylhydrazone or diphenylhydrazine with dextrosephenylmethylhydrazone. Glyoxalphenylosazone and phenylmethylhydrazine acetate yield glyoxalphenylmethylosazone. Phenylglucosazone and phenylmethylhydrazine yield the mixed osazones melting at 205°.

J. J. S.

Separation and Isolation of Reducing Sugars by means of Aromatic Hydrazines. EMIL VOTOČEK and R. VONDRÁČEK (*Ber.*, 1904, 37, 3854—3858).—The sugars contained in mixtures may readily be separated and isolated in the form of hydrazones by the addition of first one aromatic hydrazine and then a second. When an acetic acid solution of phenylhydrazine is added to an aqueous solution

containing both *d*-mannose and *d*-galactose, pure *d*-mannosephenylhydrazone is precipitated, and, on the addition of phenylmethylhydrazine to the filtrate, galactosephenylmethylhydrazone crystallises out. *d*-Galactose and dextrose can be separated by first adding phenylmethylhydrazine and then phenylhydrazine to the filtrate. *d*-Arabinose and dextrose, rhodeose and dextrose can be separated in exactly the same way, and *d*-mannose and *d*-arabinose or *d*-mannose and rhodeose by first adding phenylhydrazine and then phenylmethylhydrazine to the filtrate. Galactose and rhamnose may be separated by the aid of phenylmethylhydrazine alone, as rhamnosephenylmethylhydrazone is very readily soluble in dilute alcohol.

Arabinosediphenylhydrazone and a small amount of galactosephenylmethylhydrazone have been obtained from the hydrolytic products of "arabic acid." Mannose and dextrose could not be detected. Arabinose, galactose, and dextrose can be detected in the hydrolytic products of gum arabic, but no mannose.

Hydrolysed coffee beans yield mannosephenylhydrazone, arabinosediphenylhydrazone, and galactosephenylmethylhydrazone. J. J. S.

Relation between Quinonehydrazones and *p*-Hydroxyazo-compounds. I. Constitution of the so-called Quinonemonosemicarbazones. WALTHER BORSCHE [with T. ZELLER] (*Annalen*, 1904, 334, 143—200).—Since it would seem probable that the *p*-hydroxyazo-compounds would exist in the isomeric quinonehydrazone form when the azo-group is linked not with two similar groups, as, for example, two phenyl groups, but with two dissimilar groups, one aromatic, and the other of some different character, a series of quinonemonophenylcarbamic hydrazones have been prepared and studied.

Benzoquinonephenylcarbamic hydrazone (p-*hydroxybenzeneazoformanilide*), $OH\cdot C_6H_4\cdot N\colon N\cdot CO\cdot NHPh$ or $O\colon C_6H_4\colon N\cdot NH\cdot CO\cdot NHPh$, prepared from benzoquinone and the hydrochloride of phenylcarbamic hydrazide, crystallises in yellowish-red prisms, melting and decomposing at 185°, and is soluble in dilute alkali hydroxides and concentrated acids; the *sodium* salt is a dark red, crystalline mass. Phenylhydrazine acts as a reducing agent, converting the *p*-hydroxybenzeneazoformanilide into the p-*hydroxyphenylhydrazide* of *phenylcarbamic acid*, $OH\cdot C_6H_4\cdot NH\cdot NH\cdot CO\cdot NHPh$, which is also produced by reduction with zinc dust and acetic acid; it crystallises in needles melting and decomposing at 207°, and is reconverted by the air into the azo-derivative. Semicarbazide yields a *disemicarbazone*,

$$NH_2\cdot CO\cdot NH\cdot N\colon C_6H_4\colon N\cdot NH\cdot CO\cdot NHPh,$$

in the form of a red, crystalline powder, melting and decomposing at 242° and soluble in alkali hydroxides. Phenylsemicarbazide produces the *quinonediphenylsemicarbazone*, $C_6H_4(\colon N\cdot NH\cdot CO\cdot NHPh)_2$, which decomposes at 249—250°. Neither of the reactions just mentioned throws any decisive light on the constitution of the hydroxyazo-compound, since *p*-ethoxybenzeneazoformanilide behaves in an exactly similar manner. On brominating *p*-hydroxybenzeneazoformanilide in acetic acid solution in the presence of sodium acetate, 4-*hydroxy*-3 : 5-*dibromobenzeneazoformanilide*, $OH\cdot C_6H_2Br_2\cdot N\colon N\cdot CO\cdot NHPh$,

is obtained as yellow needles melting and decomposing at 226—227°; when decomposed by alkali hydroxides, it yields 2 : 6-dibromophenol (m. p. 56°). This reaction points to the original *p*-hydroxybenzeneazoformanilide being a hydroxy-derivative and not a quinone; the latter compound would have yielded a *s*-tribromo-derivative, the bromine atoms being in the aniline nucleus. The behaviour with benzenesulphinic acid is also in harmony with this view, since an additive compound is formed which is decomposed even by cold alkali hydroxides into its components, and therefore has the constitution $OH\cdot C_6H_4\cdot N(SO_2Ph)\cdot NH\cdot CO\cdot NHPh$; it forms colourless needles melting and decomposing at 166—167°. An isomeride, $SO_2Ph\cdot C_6H_3(OH)\cdot N:N\cdot CO\cdot NHPh$, is produced when 2 : 4-dihydroxydiphenylsulphone is oxidised and then treated with phenylsemicarbazide in alcoholic solution; it crystallises in yellowish-brown needles melting and decomposing at 195—196°.

Quinonecarbamic hydrazone (p-*hydroxybenzeneazoformamide*),
$$OH\cdot C_6H_4\cdot N:N\cdot CO\cdot NH_2,$$
is prepared by the action of semicarbazide on quinone at 0°, and crystallises in yellow needles decomposing at 178°.

4-*Hydroxy*-3 : 5-*dibromobenzeneazoformamide*,
$$OH\cdot C_6H_2Br_2\cdot N:N\cdot CO\cdot NH_2,$$
forms yellow needles melting and decomposing at 225°, dissolves in alkali hydroxides with a yellow coloration, and is decomposed on heating, 2 : 6-dibromophenol being produced.

p-*Ethoxybenzeneazoformanilide*, $OEt\cdot C_6H_4\cdot N:N\cdot CO\cdot NHPh$, is prepared either by ethylating *p*-hydroxybenzeneazoformanilide or by condensing *p*-ethoxyphenylhydrazine with phenylcarbimide and oxidising the *product*, $OEt\cdot C_6H_4\cdot NH\cdot NH\cdot CO\cdot NHPh$ (crystallising in needles melting at 137—138°), with chromic acid; it forms red plates melting at 139—140°, and is reduced by phenylhydrazine. Both semicarbazide and phenylsemicarbazide effect the elimination of the ethoxy-group and convert it into the compound above mentioned. With benzenesulphinic acid, the *additive product*, crystallising in white needles and melting and decomposing at 180°, is obtained. *Carbamino*-p-*ethoxyphenylhydrazide*, $OEt\cdot C_6H_4\cdot N_2H_2\cdot CO\cdot NH_2$, prepared from *p*-ethoxyphenylhydrazine and potassium cyanate, crystallises in colourless leaflets which redden in the air and melt and decompose at 190°, and when oxidised by chromic acid are converted into p-*ethoxybenzeneazoformamide*, $OEt\cdot C_6H_4\cdot N:N\cdot CO\cdot NH_2$, which forms orange-red crystals melting and decomposing at 164—165°.

p-*Benzoxybenzeneazoformamide*, $OBz\cdot C_6H_4\cdot N:N\cdot CO\cdot NH_2$, crystallises in orange-red leaflets, melting and decomposing at 191°. Although reduced by phenylhydrazine, it is not acted on by semicarbazide and is less reactive than the corresponding ethoxy-compound. p-*Benzoxybenzeneazoformanilide* forms yellow leaflets melting at 168—169°, dissolves in sulphuric acid with a red coloration, and yields a colourless *additive* product with benzenesulphinic acid, which softens at 140°, and is decomposed at 185°. When the *p*-benzoxy-compound is reduced by phenylhydrazine or zinc dust and acetic acid, the *benzoate* of phenylcarbamino-*p*-hydroxyphenylhydrazide, $OBz\cdot C_6H_4\cdot N_2H_4\cdot CO\cdot NHPh$, is obtained as colourless crystals melting at 203—204°.

Although it was possible that toluquinone and phenylsemicarbazide hydrochloride should react giving two isomerides, only one, o-*cresol*-5-*azoformanilide*, $OH\cdot C_6H_3Me\cdot N\colon N\cdot CO\cdot NHPh$, is obtained as dark red crystals melting and decomposing at 198—199°. Since it only yields a monobromo-derivative, 3-*bromo*-o-*cresol*-5-*azoformanilide*,

$$C_{14}H_{12}O_2N_3Br,$$

a yellow, crystalline precipitate melting at 212—213°, which can also be obtained by condensation of phenylsemicarbazide with 5-bromotoluquinone, these substances have the constitution here ascribed to them. The azocresol combines with phenylsemicarbazide, yielding the toluquinonediphenylsemicarbazone, $C_{21}H_{20}O_2N_6$, which is a red, crystalline powder decomposing at 246°. The *additive* compound with benzenesulphinic acid, $C_{20}H_{19}O_4N_3S$, is colourless, melts and decomposes at 153—154°, and is easily decomposed by alkali hydroxides. The *benzoyl* derivative, $OBz\cdot C_6H_3Me\cdot N\colon N\cdot CO\cdot NHPh$, forms reddish-yellow prisms melting and decomposing at 150°.

Thymoquinone and phenylsemicarbazide yield the single *azoformanilide*,

$OH\cdot C_6H_2MePr^{\beta}\cdot N : N\cdot CO\cdot NHPh$ [Me : Pr^{β} : (OH) : N_2 = 1 : 4 : 3 : 6], which crystallises in dark yellow needles melting at 179—180° and behaves in an analogous manner to the corresponding benzene and toluene derivatives. It combines with phenylsemicarbazide, forming *thymoquinonediphenyldisemicarbazide*, $C_{24}H_{26}O_2N_6$, a dark yellow, crystalline powder decomposing at 242°, and with benzenesulphinic acid yields an *additive* product, $C_{23}H_{25}O_4N_3S$, which decomposes at 125—130°. When brominated in acetic acid solution in the presence of sodium acetate, a *monobromo*-derivative, $C_{17}H_{18}O_2N_3Br$, is obtained, crystallising in yellow needles melting at 203°; it is also prepared from 6-bromothymoquinone and phenylsemicarbazide.

α-Naphthaquinone and phenylsemicarbazide yield the slightly soluble 1-*hydroxynaphthalene*-4-*azoformanilide*, $OH\cdot C_{10}H_6\cdot N\colon N\cdot CO\cdot NHPh$, crystallising in greenish-yellow needles melting and decomposing at 235°. Its p-*ethoxy*-derivative, $OEt\cdot C_{10}H_6\cdot N\colon N\cdot CO\cdot NHPh$, forms yellowish-white needles melting at 238°, and its *benzoyl* derivative yellow needles melting and decomposing at 230°. On bromination, the hydroxy-derivative yields 2-*bromo*-1-*hydroxynaphthalene*-4-*azoformanilide*, which crystallises in yellow needles melting and decomposing at 250° and is identical with the material prepared from bromonaphthaquinone.

β-Naphthaquinonephenylsemicarbazone is a red, insoluble, crystalline powder melting at 250—251°.

From the results of the investigation, the conclusions are drawn that the condensation products of quinones and carbamic hydrazides are not quinonehydrazones, but *p*-hydroxyazo-derivatives: that the tendency of hydroxyazo-derivatives is not to pass into hydrazones, but in the reverse direction: that the azoformanilide compounds herein described possess in a higher degree than other hydroxyazo-derivatives the power of behaving as quinone derivatives, thereby demonstrating the influence of the group combined with the azo-group. K. J. P. O.

s-Dibenzoylhydrazide and Azodibenzoyl. ERNST MOHR (*J. pr. Chem.*, 1904, [ii], 70, 281—302).—*s*-Dibenzoylhydrazide is

oxidised to benzoic acid and nitrogen by calcium hypochlorite, potassium or sodium hypobromite, or potassium tri-iodide, ferricyanide, or permanganate, in aqueous solution in presence of an excess of an alkali hydroxide. Azodibenzoyl, benzoic acid, and nitrogen are formed by oxidation of *s*-dibenzoylhydrazide with potassium tri-iodide, a faintly alkaline hypobromite, or acidified calcium hypochlorite in presence of a limited amount of alkali hydroxide, or with potassium ferricyanide or permanganate in presence of a limited quantity of alkali hydroxide and of ether.

Azodibenzoyl (Stollé and Benrath, Abstr., 1900, i, 531 ; this vol., i, 935) is reduced when heated with benzaldehyde at 125—135° to *s*-dibenzoylhydrazide.

Tribenzoylhydrazide yields *s*-dibenzoylhydrazide when treated with dilute aqueous hydroxides, and is easily oxidised therefore by alkaline potassium permanganate, tri-iodide, or ferricyanidide.

s-Benzoylphenylhydrazine is oxidised to phenylazobenzoyl by the action of iodine and sodium hydroxide solution on its ethereal solution.

G. Y.

Crystallographic Properties of *s*-Dibenzoylhydrazide and of Benzamide. Ernst Mohr (*J. pr. Chem.*, 1904, [ii], 70, 303—312). —*s*-Dibenzoylhydrazide crystallises from its hot saturated solution principally in slender needles, but also in monoclinic prisms. The amount of the monoclinic form is increased if a cold saturated solution is allowed to evaporate whilst cooled, and it is obtained free from the needles if an aqueous solution of the sodium derivative of *s*-dibenzoylhydrazide is left in a test-tube closed by a plug of cotton-wool. Both forms melt at 237—239°. If a suspension of both crystalline forms in alcohol is shaken for 3 days at 25°, the monoclinic crystals are converted into the needles. The needles are not converted into the monoclinic prisms when allowed to remain in contact with an excess of the latter in alcoholic suspension at 25° for 14 days or at 10—25° for a year.

Contrary to Wöhler and Liebig's statement (*Annalen*, 1832, 3, 270), aqueous solutions of benzamide deposit, on cooling, always triclinic (?) needles which change into stable monoclinic plates the more rapidly the higher the temperature of deposition. Solutions of benzamide in benzene, toluene, or xylene show the same behaviour. Triclinic (?) benzamide changes into the monoclinic form at 0° ; the residue from an aqueous solution, when evaporated in a current of hydrogen at 97—98°, consists of monoclinic benzamide. Both crystalline forms of benzamide melt at 126—128°. When benzamide is heated at 135—140° in a sealed capillary tube, the small drops of molten substance crystallise, on cooling, in needles which in the course of some weeks change into monoclinic plates. G. Y.

2 : 4 : 6-Trichloropyrimidine. Siegmund Gabriel and James Colman (*Ber.*, 1904, 37, 3657—3658).—A more convenient method of obtaining trichloropyrimidine than previously described (Abstr., 1901, i, 168) consists in digesting barbituric acid with phosphorus oxychloride at 130—140°, distilling the mass in a vacuum at 190°, and

subsequently fractionally distilling. In this way, about 80 per cent. of the theoretical quantity is obtained. E. F. A.

2 Methylpyrimidine. SIEGMUND GABRIEL (*Ber.*, 1904, 37, 3638—3643. Compare Abstr., 1902, i, 498).—6-*Hydroxy-2-methylpyrimidine*, $CMe \lessdot \genfrac{}{}{0pt}{}{N—CH}{NH\cdot CO} \gtrdot CH$, prepared by the condensation of acetamidine with ethyl formylacetate, crystallises from benzene in bundles of needles melting at 212° or from water with $1\frac{1}{2}H_2O$ in glistening, rhombic plates; the *hydrochloride* forms colourless needles, the *silver* salt a colourless, amorphous powder soluble in ammonia, and the *platinichloride* crystallises in octahedra. 6-*Chloro-2-methylpyrimidine*, formed by the action of phosphorus oxychloride on the foregoing compound, boils at 168° under 768 mm. pressure and crystallises in colourless rhombs melting at 59—60°. Ammonia in alcoholic solution converts it into 6-*amino-2-methylpyrimidine*, crystallising from acetone in colourless rhombs melting at 205° and forming a *nitrate*, which crystallises in prisms and melts and decomposes at 213—214°, an *aurichloride* crystallising in needles which melt and decompose at 203°, and a *platinichloride* melting and decomposing at 248—250°. It is reduced by zinc dust to 2-*methylpyrimidine*, $CMe \lessdot \genfrac{}{}{0pt}{}{N\cdot CH}{N:CH} \gtrdot CH$, which boils at 138° under 758 mm. pressure, melts at −4—5°, and forms a *hydrochloride* crystallising in flat needles or rhombic plates, a *picrate* crystallising in yellow needles which sinter at 97° and melt at 106—107°, a *platinichloride* crystallising in short, yellow rods, and an *aurichloride* which crystallises in pointed needles melting at 124°.
E. F. A.

Quinazoline. II. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1904, 37, 3643—3656. Compare Abstr., 1903, i, 445).—Quinazoline is best prepared by reduction of *o*-nitrobenzylamine with hydrogen iodide and red phosphorus to 2-aminobenzylamine, combination of this with formic acid to form dihydroquinazoline, and subsequent oxidation to quinazoline, $C_6H_4 \lessdot \genfrac{}{}{0pt}{}{CH:N}{N{=}CH}$. In a similar manner, *o*-nitrobenzylmethylamine can be reduced to *o*-aminobenzylmethylamine, and this combined with formic acid to yield 3-*methyldihydroquinazoline*, $C_6H_4 \lessdot \genfrac{}{}{0pt}{}{CH_2\cdot NMe}{N{=}CH}$, which crystallises in prisms sintering at 80° and melting at 91—92°, boils at 309° under 766 mm. pressure, and forms a *picrate* crystallising in silky, yellow needles melting at 193—194°, a *platinichloride* crystallising in brownish-yellow needles, and a crystalline *hydriodide*.

Quinazoline is oxidised by permanganate to *pyrimidine*-5 : 6-*dicarboxylic acid*, $C_4N_2H_2(CO_2H)_2,H_2O$, which on heating becomes brown at 180° and melts and decomposes at 265°; the *ammonium* salt crystallises in long needles, melting and decomposing at 215°; the *copper* salt forms bright blue crystals and the *silver* salt a heavy, crystalline, sparingly soluble powder.

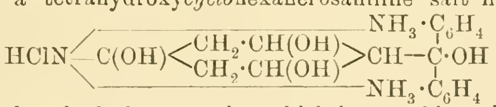
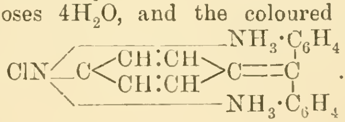
On distillation in a vacuum, pyrimidinedicarboxylic acid is converted

into *pyrimidine-5-carboxylic acid*, which crystallises in platelets sintering at 245° and melting at 270° to a dark red liquid.

Quinazoline combines with methyl iodide to form *quinazoline-3-methiodide*, a yellow, crystalline solid which, on heating, darkens at 115°, melts at 125—127°, and decomposes at 128°. On treatment with alkali, it is converted into *quinazoline-3-methylium hydroxide*, $C_6H_4<\begin{matrix}CH:NMe\cdot OH \\ N{=}CH\end{matrix}$, which crystallises in rhombs melting at 163—165° to a brown liquid. On distillation with potassium hydroxide, an oil, $C_9H_{10}N_2$, and a base, $C_{15}H_{15}N_3$, were obtained. The oil is proved to be *o-aminobenzylidenemethylamine*, $NH_2\cdot C_6H_4\cdot CH:NMe$, and was prepared synthetically from *o*-aminobenzaldehyde and methylamine, whilst the *base*, which crystallises in rhombic plates melting at 188—190°, is shown to have the constitution

$$NMe:CH\cdot C_6H_4\cdot N:CH\cdot C_6H_4\cdot NH_2.$$

It forms a chrome-red *hydrochloride*, $C_{15}H_{15}N_3,2HCl$. E. F. A.

Constitution of the Rosaniline Salts and the Mechanism of their Formation. Jules Schmidlin (*Compt. rend.*, 1904, **139**, 602—604. Compare this vol., i, 698, 786, 943, 944).—When rosanilinecarbinol dissolves in dilute acetic acid, there is a development of heat and the formation of a colourless liquid, followed by an absorption of heat and the formation of a coloured liquid. In explanation of these phenomena, the author suggests that in the first stage a triazine ring is formed by the migration of the hydrogen atoms from one amino-group to the other two and the subsequent linking of the nitrogen atoms; at the same time, the interior benzene ring becomes saturated by absorbing three mols. of water, and the unstable colourless liquid is therefore a tetrahydroxy*cyclo*hexanerosaniline salt having the constitution  ; in the second stage, the hexahydrobenzene ring, which is unstable under the influence of the triazine ring, loses $4H_2O$, and the coloured compound has the quinonoid structure  . M. A. W.

The Tetrahydroxy*cyclo*hexanerosanilines. Jules Schmidlin (*Compt. rend.*, 1904, **139**, 676. Compare this vol., i, 698, 785, 943, 944).—The colourless oxalate of malachite-green,

$$C_{23}H_{26}ON_2,2C_2H_2O_4,3H_2O,$$

described by Lambrecht and Weil (compare this vol., i, 877), loses $4H_2O$ at 70° and becomes the coloured oxalate of malachite-green, $C_{23}H_{24}N_2,2C_2H_2O_4$; these facts afford a further confirmation of the quinonoid constitution of the coloured rosaniline salts. M. A. W.

[Hydroxyphenyl Derivatives of 4 : 4′-Diaminodiphenylamine.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 153130 and 153994).—On oxidising a mixture of 1 mol. of 4 : 4′-diamino-

diphenylamine, and 2 mols. of phenol with sodium dichromate in hydrochloric acid solution, an *indophenol*,

$$\begin{matrix}O\text{——} \\ | \\ C_6H_4\end{matrix}\!\!>N\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot N<\!\!\begin{matrix}O \\ | \\ C_6H_4\end{matrix},$$

is obtained. Alcoholic sodium sulphide reduces it to *di*-p-*hydroxyphenyl*-4 : 4′-*diaminodiphenylamine*, $NH(C_6H_4\cdot NH\cdot C_6H_4\cdot OH)_2$, forming colourless leaflets melting at 208°, and dissolving readily in alcohol, sparingly in benzene.

When 1 mol. of phenol is employed, an *indophenol* is also obtained, yielding on reduction p-*hydroxyphenyl*-4 : 4′-*diaminodiphenylamine*, $OH\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot NH_2$, crystallising from water and melting at 185°. Hydrochloric acid and sodium hydroxide dissolve it to colourless solutions, the alkaline solution becoming blue in air.

Both the indophenols and their reduction products yield blue dyes on fusion with sulphur and sodium sulphide. C. H. D.

[Action of Sulphur on Tolylenedicarbamide.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 153916).—On fusing tolylenedicarbamide (prepared from 1-tolylene-2 : 4-diamine and potassium cyanate) with sulphur at 200—230°, an orange dye is obtained, dissolving in hot solutions of alkali sulphides or in concentrated sodium hydroxide. C. H. D.

2 : 4 : 2′ : 4′-Tetra-aminostilbene. Richard Escales (*Ber.*, 1904, 37, 3598—3600).—2 : 4 : 2′ : 4′-Tetranitrostilbene, prepared by Krassusky's method (*J. Russ. Phys. Chem. Soc.*, 1895, 27, 335), may be reduced in glacial acetic acid solution by means of stannous chloride, the temperature rising to 60—80°. The orange solution of the tin salt is rendered alkaline with dilute sodium hydroxide and extracted with ethyl acetate, the upper layer then being distilled in a yellow glass flask in a current of carbon dioxide. 2 : 4 : 2′ : 4′-*Tetra-aminostilbene*, $C_{14}H_{16}N_4$, separates from amyl alcohol in an atmosphere of carbon dioxide in microscopic, brown crystals and melts at about 191°. Its solutions readily darken in air or light. The *hydrochloride* may be precipitated by hydrogen chloride. C. H. D.

Fluorindines of the Naphthalene Series. Rudolf Nietzki and August Vollenbruck (*Ber.*, 1904, 37, 3887—3891).—The method of Nietzki and Slaboszewicz (Abstr., 1902, i, 125) for the synthesis of fluorindines may also be applied to naphthalene derivatives.

Aminonaphthyl-3-chloro-4 : 6-dinitroaniline,

$$NH_2\cdot C_{10}H_6\cdot NH\cdot C_6H_2Cl(NO_2)_2,$$

prepared by boiling $\alpha\beta$-naphthylenediamine with dichlorodinitrobenzene and sodium acetate, forms brownish-red leaflets melting at 232° and dissolves sparingly in alcohol, readily in amyl alcohol or xylene. The *acetyl* derivative forms bright yellow needles and dissolves only in nitrobenzene. Boiling with amyl alcohol and sodium carbonate forms *diaminodinaphthyldinitro*-m-*phenylenediamine*,

$$C_6H_4(NO_2)_2(NH\cdot C_{10}H_6\cdot NH_2)_2,$$

crystallising from pyridine and melting at about 300°. Stannous chloride reduces it to *diaminodinaphthyltetra-aminobenzene*,

$$C_6H_4(NH_2)_2(NH{\cdot}C_{10}H_6{\cdot}NH_2)_2,$$

which is readily oxidised by air or ferric chloride, forming the orange *hydrochloride* of *aminonaphthyldiaminonaphthaphenazine*,

$$C_{10}H_6{<}{\overset{-N-}{\underset{NH}{}}}{>}C_6H_2{<}{\overset{NH{\cdot}C_{10}H_6{\cdot}NH_2}{\underset{NH}{}}}.$$

On heating with dilute hydrochloric acid, *naphthafluorindine*,

$$C_{10}H_6{<}{\overset{-N-}{\underset{NH}{}}}{>}C_6H_2{<}{\overset{NH}{\underset{N-}{}}}{>}C_{10}H_6,$$

is obtained. The base forms red solutions; its salts are sparingly soluble, and form blue solutions. The solution in concentrated sulphuric acid is blue and non-fluorescent.

Aminonaphthylaminophenyldinitro-m-*phenylenediamine*, prepared from aminonaphthylchlorodinitroaniline and *o*-phenylenediamine, crystallises in leaflets, melts at 259°, and yields a *tetra-aminobenzene* derivative on reduction. Oxidation then forms *phenonaphthafluorindine*, $C_6H_4{<}{\overset{-N-}{\underset{NH}{}}}{>}C_6H_2{<}{\overset{NH}{\underset{N-}{}}}{>}C_{10}H_6$, dissolving in alcohol to a yellow solution with red fluorescence. The hydrochloride forms a blue solution. C. H. D.

Tetra-aminocarbazole. Richard Escales [and K. Wolgast] (*Ber.*, 1904, 37, 3596—3598).—Ciamician and Silber have shown (Abstr., 1882, 1103) that four isomeric tetranitrocarbazoles are produced in the action of nitric acid on carbazole. The authors describe the separation of the isomerides, and obtain considerably lower melting points than Ciamician and Silber (α, 285—286°; β, 273°; γ, 275°; the δ-compound was not obtained in a crystalline form: C. & S. gave α, 308°; β, 320°; and γ, 275°).

Stannous chloride reduces the ice-cold solutions of the tetranitro-compounds in glacial acetic acid, and after decomposing the tin salt with hydrogen sulphide, filtering, and passing a current of hydrogen chloride through the filtrate, the *hydrochloride* of the corresponding *tetra-aminocarbazole*, $C_{12}H_{13}N_5,4HCl$, is obtained. The α-, β-, and γ-hydrochlorides crystallise from dilute alcohol on the addition of ether in greyish-white needles; the δ-compound forms yellow crystals.

C. H. D.

[*p*-Diazonium Compounds of Phenylalkylnitrosoamines.] Badische Anilin- & Soda-Fabrik (D.R.-P. 154336).—*p*-Aminoalkylanilines (1 mol.) react with sodium nitrite (2 mols.) to form the *p*-diazonium compounds of the corresponding phenylalkylnitrosoamines, which readily combine with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid in alkaline or acetic acid solution, forming violet azo-dyes. On hydrolysing with warm dilute acids, the nitroso-group is removed, and blue azo-dyes are obtained, identical with those prepared from 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid and diazotised *p*-aminoalkylanilines. C. H. D.

Azo-dyes from Ethers of Diaminocresol and Chlorodiaminophenol. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 153939 and 153940).—A blue azo-dye is obtained by diazotising an ether of 2-acylamino-5-amino-*p*-cresol, combining with the sulphonic acids of 1 : 8-dihydroxynaphthalene, and removing the acyl group from the products; or by diazotising an ether of 5-nitro-2-amino-*p*-cresol, combining with the same acids, and reducing the products.

Similar dyes are obtained in the same way from ethers of 4-chloro-5-amino-2-acylaminophenol or 4-chloro-5-nitro-2-aminophenol.

The introduction of an alkyloxy-group in this way has the same effect in the production of a blue shade as the alkylation of the amino-group. C. H. D.

Influence of Unsaturated Side-chains on the tendency of Phenols to Couple, and the Colour of the resulting Oxyazo-compounds. WALTHER BORSCHE and F. STREITBERGER (*Ber.*, 1904, 387, 4116—4136).—*Benzeneazocoumaric acid*,

$$N_2Ph\cdot C_6H_3(OH)\cdot CH{:}CH\cdot CO_2H,$$

prepared from *o*-coumaric acid and phenyldiazonium chloride, is a brownish-red, crystalline powder melting and decomposing at 206°; the *acetate* crystallises in yellow plates, melting at 167—169°. *Sulphobenzeneazocoumaric acid* forms a red powder which could not be melted in a sulphuric acid bath. *Sulphobenzeneazocoumarin*, prepared by the interaction of coumarin and diazobenzenesulphonic acid, separates from hot water in reddish-yellow needles. *Benzeneazo*-m-*hydroxycinnamic acid* forms bright red crystals grouped in stars which melt at 168°. The corresponding compound of *m*-hydroxycinnamic acid and diazobenzenesulphonic acid could not be isolated; similarly, with *p*-hydroxycinnamic acid, only undefinable decomposition products were obtained.

Benzeneazomelilotic acid, $N_2Ph\cdot C_6H_3(OH)\cdot CH_2\cdot CH_2\cdot CO_2H$, crystallises from dilute alcohol in bright yellow plates melting at 130°. *Disbenzeneazomelilotic acid*, $OH\cdot C_6H_2(N_2Ph)_2\cdot CH_2\cdot CH_2\cdot CO_2H$, crystallises from alcohol in dark brown plates melting at 194°. *Sulphobenzeneazomelilotic acid*, prepared by coupling melilotic acid with diazotised sulphanilic acid, crystallises from dilute hydrochloric acid in dark red needles. *Benzeneazo*-m-*hydroxydihydrocinnamic acid*, $N_2Ph\cdot C_6H_3(OH)\cdot CH_2\cdot CH_2\cdot CO_2H$, separates in yellowish-red, silky, glistening needles which melt at 146°. *Disbenzeneazo*-m-*hydroxydihydrocinnamic acid* is a brown, crystalline powder melting at 179—180°; *sulphobenzeneazo*-m-*hydroxydihydrocinnamic acid* separates as a dark red, crystalline powder. *Benzeneazo*-p-*hydroxydihydrocinnamic acid* crystallises in red needles which melt at 140—141°; the corresponding *sulphonic acid* derivative is a dark red powder.

α-*Phenylbenzeneazocoumarin* crystallises from acetic acid in reddish-brown needles, from alcohol in orange-yellow plates which melt at 205°; the corresponding *sulphonic acid* also forms orange-yellow needles. α-Phenyl-*m*-hydroxycinnamic acid could not be brought to enter into reaction with diazo-compounds; the corresponding para-compound

forms *a-phenylbenzeneazo-p-hydroxycinnamic acid*,

$$N_2Ph\cdot C_6H_3(OH)\cdot CH:CPh\cdot CO_2H,$$

which crystallises in yellow needles melting at 247°. No corresponding compound was obtained with *p*-diazobenzenesulphonic acid.

a-Phenylbenzeneazomelilotic acid, prepared from *a*-phenylmelilotic acid and a solution of a diazo-compound, crystallises in aggregates of yellowish-red needles melting at 152—153°; the *disbenzeneazo*-compound forms a dark brown, crystalline mass melting at 223°; the *benzenesulphonic acid* derivative is dark red. *a-Phenylbenzeneazo-m-hydroxydihydrocinnamic acid* crystallises from alcohol in reddish-yellow, star-shaped needles melting at 177°. The corresponding p-*hydroxy*-compound forms yellowish-red plates melting at 159°. *Benzeneazoeugenol* crystallises in long, dark red needles melting at 76—77°, easily soluble in dilute alkaline hydroxides with a bluish-red coloration; *benzeneazoisoeugenol* is a brown, amorphous powder. E. F. A.

Diazo-compounds from Amino-α-naphtholdisulphonic Acid. Kalle & Co. (D.R.-P. 153299).—On nitrating and reducing 2 : 6-dichlorobenzenesulphonic acid, an aminosulphonic acid is obtained the diazo-derivative of which combines with 8-amino-α-naphthol-3 : 6-disulphonic acid. The aminoazo-dyes thus obtained then combine readily with diazotised amines, yielding fast diazo-colouring matters. C. H. D.

Substituted Derivatives of Phenyldiazoaminobenzene. Léo Vignon and Adolphe Simonet (*Compt. rend.*, 1904, 139, 569 571. Compare this vol., i, 637).—The following substituted derivatives of phenyldiazoaminobenzene are readily prepared by the action of diphenylamine on the corresponding substituted diazotised amine: o-, m-, and p-*nitrophenyldiazoaminobenzenes* are soluble in alcohol, ether, or benzene, insoluble in water, the first two are liquids, the third a red solid, melting at 63°; o- and m-*chlorophenyldiazoaminobenzenes* are liquids, whilst the *p*-compound melts at 20°; 2 : 4-*dichlorophenyl-1-diazoaminobenzene* is an orange-yellow solid melting at 35—40°; 1 : 3 : 5-*trichlorophenyl-2-diazoaminobenzene* is a brown solid melting at 38—39°; o-, m-, and p-*bromophenyldiazoaminobenzenes* are unstable liquids; 1 : 3-*dibromophenyldiazoaminobenzene* is a red solid melting at 80°; 1 : 3 : 5-*tribromophenyldiazoaminobenzene* is a yellow, crystalline solid melting at 48°; p-*iodophenyldiazoaminobenzene* is a deep red liquid; 2 : 4-*di-iodophenyldiazoaminobenzene* is a brown solid melting at 70°; o-*methoxyphenyldiazoaminobenzene* is a brown, crystalline solid melting at 30—32°; the corresponding para-derivative is a reddish-brown liquid. M. A. W.

The Combination of Nitrogen in Proteids. C. H. Rothera (*Beitr. chem. Physiol. Path.*, 1904, 5, 442—448. Compare Gümbel, this vol., i, 460).—From experiments made by Embden and also by the author it appears that only some 2/3 of the total amide nitrogen is driven off as ammonia when the distillation with magnesia is conducted in a vacuum at 40°; the remaining 1/3 is given off at higher temperatures.

When the acid decomposition of proteids is carried out in presence of reducing agents, for example, hydriodic acid or stannous chloride (compare Hlasiwetz and Habermann, *Annalen*, 1873, **169**, 150), the amount of monamino-nitrogen is increased, and that of the diamino-nitrogen diminished.

The values obtained for the nitrogen in serum albumin are: amide, 1·04; melanin, 0·26; monoamino-, 9·98; diamino-, 5·21 per cent. (compare Gümbel).

For ichthyn from the eggs of *Torpedo marmorata*, the following numbers were found: total nitrogen, 15·7; amide, 1·32; melanin, 0·198; monoamino-, 9·58; diamino-, 3·99 per cent. These numbers differ slightly from those obtained for ichthyn from the sturgeon. J. J. S.

Hydrolysis of Proteids. EMIL FISCHER and EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1904, **42**, 540—544).—The tyrosine obtained by the hydrolysis of casein (Abstr., 1901, i, 780) is highly impure and can only be obtained pure after repeated crystallisations from water. Two impurities which have been isolated are lysine and a *diaminotrihydroxydodecanoic acid*, $C_{12}H_{26}O_5N_2$, both of which are more readily soluble in water than tyrosine. The new acid is isolated from the mother liquors by precipitation with phosphotungstic acid, and is purified by means of the *hydrochloride*, which crystallises from concentrated hydrochloric acid in slender needles. The acid turns brown, melts, and decomposes at about 255°; it is optically active, $[\alpha] - 9°$, and is readily soluble in dilute mineral acids. The *copper* salt, $C_{12}H_{24}O_5N_2Cu$, crystallises in pale blue plates. The yield of acid depends to a large extent on the details of the method of hydrolysis.

Serin has been detected among the products formed by the hydrolysis of gelatin with acids. J. J. S.

Proteids of Wheat Gluten. I. Proteids of Wheat Meal. JOSEF KÖNIG and P. RINTELEN (*Zeit. Nahr. Genussm.*, 1904, **8**, 401—407).—Fresh gluten (2—3 kilos.), well washed with water, was made into threads by means of a meat press and treated successively with absolute alcohol and ether to remove water and fat. The small amount of proteid dissolved by the alcohol was recovered by precipitating with ether, and after being treated with alcohol-ether was added to the rest. The whole was then put into a long linen bag and suspended in a cylinder containing 65 per cent. alcohol which was frequently renewed. Finally, the bag was gently pressed. The clear extract was mixed with 97 per cent. alcohol (about 6·25 litres to 2·5 litres of extract) so as to raise the strength to 85—90 per cent., and the whole immersed in ice-water. The precipitate obtained in this manner, consisting of gliadin and mucedin, is again dissolved in 65 per cent. alcohol, half of which is distilled off. On cooling, the gliadin separates, adhering to the flask. The alcohol is poured off, and distilled until two-thirds remain and allowed to cool. The precipitate thus obtained is neglected, being possibly a mixture of gliadin and mucedin. The filtrate from it, evaporated to dryness, yielded a considerable amount of pure mucedin.

The first filtrate (from the gliadin and mucedin) contained the

gluten-fibrin. This is obtained by distilling off the alcohol and extracting the residue with water, drying, and extracting with ether. It is then dissolved in alcohol containing a little potassium hydroxide, shaken several times with ether, the slightly alkaline solution exactly neutralised with hydrochloric acid, and evaporated to dryness. This treatment is necessary to remove completely the sugar and fat.

The average composition of the products was found to be as follows:

	C.	H.	N.	S.	O.
1. Gluten-fibrin......	55·30	8·17	16·86	1·07	19·73
2. Gliadin	52·70	7·62	17·77	0·95	20·96
3. Mucedin	53·33	8·07	16·83	0·78	20·99

The three substances dissolve respectively in 88—90, 60—70, and 30—40 per cent. alcohol. N. H. J. M.

Decomposition of Pseudomucin by Concentrated Boiling Acids. I. J. Otori (*Zeit. physiol. Chem.*, 1904, **42**, 453—460).—Pseudomucin (Steudel, Abstr., 1902, i, 399) containing some 2·22 per cent. of ash was heated on the water-bath with 33·3 per cent. sulphuric acid and the mixture ultimately boiled during 12 hours. On dilution, only a small amount of humin substance was precipitated. The filtrate was extracted with ether in a Kutscher-Steudel extractor and the ethereal solution tested for acids. The sulphuric acid solution was examined for bases. The following is a complete list of the substances isolated: ammonia, 0·7517; guanidine, 0·0393; arginine, 0·2875; lysine, 2·6389; tyrosine, 1·089; leucine, 4·677; oxalic acid, 0·1275; lævulic acid, 1·971; a-reducing sugar calculated as dextrose, 0·7333; and humin, 6·056 per cent. J. J. S.

Lecithin. Richard Willstätter and Karl Lüdecke (*Ber.*, 1904, **37**, 3753—3758. Compare Ulpiani, Abstr., 1901, i, 491, 498).—The hydrolysis of lecithin with cold barium hydroxide solution gives an optically active glycerophosphoric acid which probably has the formula $OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OPO_3H_2$; lecithin thus appears to have the constitution attributed to it by Ulpiani. It is not decided whether Pelouze's glycerophosphoric acid, to which the same formula has been given, is the racemic form of the active acid obtained from lecithin.

Barium glycerophosphate from lecithin, $C_3H_7O_6PBa,\frac{1}{2}H_2O$, is precipitated from its aqueous solution on adding alcohol as a flocculent mass; different values of $[\alpha]_D$ varying from $-0·68°$ to $-1·712°$ were observed. The corresponding *calcium* salt forms small needles, has the composition $C_3H_7O_6PCa,\frac{3}{4}H_2O$, and $[\alpha]_D$ $-0·68°$ to $-2·09°$. The barium salt of the synthetical acid separates with $1H_2O$, but is not crystalline; the calcium salt of the same acid forms small needles with $1\frac{1}{2}H_2O$. The calcium salt of the natural acid has a solubility of 2·62 grams per 100 c.c. of saturated solution at 18°, the solubility of the analogous synthetic salt being 5·54. W. A. D.

Blood Pigments. P. P. Laidlaw (*J. Physiol.*, 1904, **31**, 464—472).—Hoppe-Seyler showed that the removal of iron from hæmatin in the absence of reducing agents is difficult. This was denied by

Nencki and Sieber. The present experiments show that the addition of mineral acids (except concentrated sulphuric acid) to oxyhæmoglobin produces hæmatin, but to hæmoglobin produces hæmatoporphyrin. In the absence of oxygen, even 2 per cent. hydrochloric acid produces hæmatoporphyrin with an intermediate formation of hæmochromogen; in the presence of oxygen, the concentrated acid, aided by heat and pressure, is necessary. Oxygen confers stability on the iron of the blood pigment. It further appears that the hæmatoporphyrin group is present as such in hæmoglobin, and hæmatoporphyrinuria becomes intelligible if it is considered that the body-cells deal with the reduced pigment. If hæmatoporphyrin is dissolved in dilute ammonia and warmed with Stokes's fluid and a little alkaline hydrazine hydrate, the iron is replaced, hæmochromogen reappears, and by shaking this with air, hæmatin presenting all the characters of the natural pigment is obtained. Hæmin crystals were, however, not readily obtained; this is true also for pure natural hæmatin: an important factor in crystal formation is the union with proteid, and it is probable that the acetyl introduced takes the place of the globin group. If hæmatoporphyrin, dissolved in ammonia, is boiled with cuprammonium solution, a pigment having all the characters of turacin is formed at once. A cobalt hæmatoporphyrin was also obtained. Bilirubin does not form an iron compound in this way, but it does yield one with copper; the solution is green in alkaline and purple in acid solution. This may be employed as a test for bilirubin. W. D. H.

Constitution of Histidine. I. Hermann Pauly (*Zeit. physiol. Chem.*, 1904, 42, 508—518. Compare Fränkel, Abstr., 1903, i, 650).—The presence of a carboxylic group in the histidine molecule has been confirmed by esterification with methyl alcohol and hydrochloric acid. The *methyl ester dihydrochloride*, $C_5H_8N_3{\cdot}CO_2Me,2HCl$, crystallises from methyl alcohol in flat, rhombic prisms melting and decomposing at 196° and readily soluble in water. The free ester is a viscid oil. Fränkel has already proved the presence of an amino-group in the histidine molecule, and as it is now shown that histidine yields a dinaphthalene-β-sulphone derivative, an imino-group must also be present. The *disulphone*, $C_6H_7O_2N_3(SO_2{\cdot}C_{10}H_7)_2$, crystallises from 60 per cent. alcohol in slender, felted needles which are insoluble in water.

Histidine reacts with diazobenzenesulphonic acid in the presence of alkali, yielding a dark cherry-red dye which turns orange-coloured when acidified. This is an extremely delicate reaction, and can be made use of in testing for histidine if tyrosine is known to be absent. None of the other hydrolytic products gives a similar reaction. All proteids which yield histidine and tyrosine on hydrolysis, for example, sturin, histon, edestin, and casein, give the red colour with diazobenzenesulphonic acid, whereas proteids which do not yield histidine and tyrosin on hydrolysis do not give the coloration. The stability of histidine towards acid oxidising agents (nitric acid) is used as an argument against Fränkel's formula, which contains a dihydropyrimidine ring, and the following formula is suggested:

$$CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}C{<}\begin{matrix}NH{\cdot}CH\\ \vert\\ CH{=}N\end{matrix}.$$

This contains the iminazole ring, and the properties of histidine are in agreement therewith. J. J. S.

Constitution and Synthesis of Adrenaline. ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1904, 6, 92—93).—Pauly (this vol., i, 128), discussing the constitution of adrenaline, describes it as a secondary base having the formula $C_6H_4(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NHMe$ or $C_6H_4(OH)_2 \cdot CH(NHMe) \cdot CH_2 \cdot OH$ [$CH : (OH)_2 = 1 : 3 : 4$]. The present research lends support to the first of the two suggestions, a view also taken by Jowett. The material used was von Fürth's adrenaline tribenzenesulphonate (Abstr., 1903, i, 669), which is lævorotatory and contains a free aliphatic hydroxyl group; by oxidation, a substance is formed which contains the same number of carbon atoms, but no asymmetric carbon atom. This testifies to its ketonic character. By further oxidation, another substance is obtained also with the same number of carbon atoms, which is a substituted acid amide. The names and formulæ ascribed to the grouping in the two products are respectively *adrenalone*, $C_6H_4(OH)_2 \cdot CO \cdot CH_2 \cdot NHMe$, and *peradrenalone*, $C_6H_4(OH)_2 \cdot CO \cdot CO \cdot NHMe$. This is confirmed by the following attempt at synthesis. By the action of methylamine on chloracetylcatechol, a product is obtained, methylaminoacetylcatechol, which is adrenalone. The power of this synthetic adrenalone to elevate blood-pressure is very great. Further work is in progress. W. D. H.

Constitution and Synthesis of Adrenaline. HANS MEYER (*Centr. Physiol.*, 1904, 18, 501).—A claim for priority in favour of F. Stolz and W. Reser, who arrived at the same conclusions as Friedmann (see preceding abstract) by the same methods in July last.
W. D. H.

Amylase. JEAN EFFRONT (*Chem. Centr.*, 1904, ii, 767; from *Mon. Sci.*, [iv], 18, 561—565).—Asparagine acts only on the first products of the hydration of starch, and the further this has proceeded the less its influence. It does not act as an acid, and the diastatic activity is reduced by addition of acetic acid, whilst considerable amounts of asparagine act favourably. The conclusion is drawn that all amino-acids have a beneficial influence on amylase independent of temperature and degree of alkalinity. Aspartic acid has about the same effect as asparagine, whilst succinamide hinders the diastatic action.

Glycine, sarcosine, alanine, leucine, glutamic acid, hippuric acid, creatinine, and creatine all act favourably, as do also the products of the action of pepsin and trypsin on proteids. Liebig's extract has only a slight effect. N. H. J. M

Researches on Lactase. A. BRACHIN (*J. Pharm. Chim.*, 1904, [vi], 20, 300—308).—Lactase is found to be present in various plants of the orders *Rosaceæ, Cruciferæ, Cornaceæ*, and *Rutaceæ*, but was not found in the lower plants. Lactase (in two per cent. solution) ceases to be active at between 75° and 80°.

Acetic acid of the strength 2·4 per 1000 prevents the hydrolysis of lactose by lactase, whilst the hydrolysis of amygdalin by emulsin is not prevented by acid of the strength 12·0 per 1000. Sulphuric and oxalic acids of the strength 0·09 to 0·1 per 1000 and tartaric acid of the strength 7·5 per 1000 also prevent the action of lactase. G. D. L.

Studies on Enzyme Action. V. Hydrolysis of Isomeric Glucosides and Galactosides by Acids and Enzymes. E. Frankland Armstrong (*Proc. Roy. Soc.*, 1904, **74**, 188—194. Compare this vol., i, 956, 957).—The hydrolysis of 3 per cent. solutions of α-methylglucoside, β-methylglucoside, α-methylgalactoside, β-methylgalactoside, and salicin by $N/2$ hydrochloric acid has been studied at 74·1° and 74·8°. The values of the velocity constant K at 74·1°, calculated on the assumption that the change is unimolecular, are as follow: α-methylglucoside, 0·0100; β-methylglucoside, 0·0179; α-methylgalactoside, 0·0542; β-methylgalactoside, 0·0884; salicin, 0·0601. The experiments on enzyme activity have so far been confined to the hydrolysis of maltose and α-methylglucoside at 22°. When these two are hydrolysed by the same yeast extract under precisely similar conditions, the initial value of K in the case of the glucoside lies at about 0·025, in the case of maltose about 0·12 or even higher. In each case, the value of K falls off as the hydrolysis proceeds, this feature being especially noticeable in the case of the maltose, where the influence of the products of change is more obvious. The above numbers show that the enzyme is much more active than the acid in promoting hydrolysis. It is probable, however, that the enzyme owes its apparent activity to its greater affinity for the sugar, and that in reality the acid has the greater hydrolytic activity. J. C. P.

Studies on Enzyme Action. VI. Sucroclastic Action of Acids as contrasted with that of Enzymes. Part II. E. Frankland Armstrong and Robert John Caldwell (*Proc. Roy. Soc*, 1904, **74**, 195—201. Compare this vol., i, 956, 957, and preceding abstract).—When solutions of sucrose containing 171 and 342 grams per litre are hydrolysed by $N/500$ HCl at 40°, the velocity constant K increases in value during the first 4 or 5 hours of the change and then remains constant. In the first period, the change proceeds at an approximately linear rate, thus completing the analogy between acid and enzyme action (compare *loc. cit.*, 956). In both cases, when the proportion of hydrolyst is relatively small, the change is at first approximately a linear function of the time and subsequently a logarithmic function; when the proportion of hydrolyst is larger, the change is a logarithmic function throughout, which may become modified by secondary causes.

The influence of the products of change on the rate of hydrolysis of sucrose has also been studied. It appears that about the same increase in the value of K is produced by molecular quantities of dextrose and lævulose, whilst the molecular effect of the biose sucrose is about twice the molecular effect of the monose. J. C. P.

The Hydrolysis of Optically Inactive Esters by means of Enzymes. I. The Action of Lipase on Esters of Mandelic Acid. The Resolution of Inactive Mandelic Acid. HENRY D. DAKIN (*J. Physiol.*, 1903, 30, 253—263. Compare Proc., 1903, 161).—Inactive methyl, ethyl, *iso*amyl, and benzyl mandelates are hydrolysed by lipase, the dextrorotatory component being more rapidly decomposed than the lævorotatory component. A method of determining accurately the degree of hydrolysis and the optical activity of the product is described. The results are best explained on the assumption that lipase is an asymmetric compound, and forms additive compounds with the ester. These compounds not being optical antipodes are hydrolysed with unequal velocities.

Lipase was found to be without action on *l*-menthyl or *d*-bornyl mandelate. Horse serum contains a lipolytic enzyme which readily hydrolyses ethyl mandelate, giving an active product, but no such result could be obtained with pig serum, although the organs of the pig furnish specially active lipase preparations.

iso*Amyl mandelate* forms a colourless oil boiling at 164—165° under 12 mm. pressure and solidifying on cooling. C. H. D.

Decomposition of Fats by Enzymes. SERGIUS FOKIN (*Chem. Rev. Fett. Ind.*, 1904, 11, 91—92; 118—120; 139—141; 167—170; 193—195; 224—226; 244—247. Compare this vol., ii, 199, 280).—Castor oil seed was mixed with dilute sulphuric acid and almond oil, and the amount of fatty acid, produced at 25°, was estimated. Seeds from various sources, which had been kept for variable times, gave similar results.

The amount of water necessary depends on the amount of seed used. The concentration of mineral acid must be within *N*/20 and *N*/120, according as the amount of seed is between 5 and 40 per cent. With small amounts of mineral acids the process is slow, whilst with large amounts of a concentration greater than *N*/10 the action of the ferment is totally destroyed.

The percentage yield of fatty acid is increased by carefully mixing the mass, and is larger the more fat is used. Solid and rancid fats are decomposed with difficulty. The decomposition can be effected by carbonic acid or by fatty acids. The results obtained with various oils are represented by curves. The action of pancreas juice on almond oil was also examined. A. McK.

Ferment Action and Ferment Loss. H. REICHEL and KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1904, 6, 68—86).—Experiments on the velocity of rennet action shows that the loss of activity which apparently occurs after previous action is due to inclusion of some of the ferment in the cheese and whey. There is no real loss of activity associated with previous action; in other words, rennet acts as a catalytic agent. W. D. H.

Yeast Ferments. K. SHIGA (*Zeit. physiol. Chem.*, 1904, 42, 502—507. Compare Milroy, Abstr., 1897, i, 232; Jones and Partridge, this vol., i, 838).—When guanine is added to yeast extract which is

undergoing autolysis in the presence of toluene, it is found that the base is destroyed, whereas the amount of xanthine increases. The amounts of adenine and hypoxanthine vary considerably in different experiments.

Kossel and Dakin's arginase is also present in yeast extract. This has been proved by the decomposition of arginine added to the extract.

J. J. S.

Isolation of Zymase from Animal and Vegetable Tissues. PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1904, 18, 535—544. Compare Abstr., 1902, ii, 622).—A critical review of Stoklasa's work; his facts appear to be correct, but his explanation is disputed.

W. D. H.

Action of Phosphorus Chlorides on Organomagnesium Derivatives of the Aromatic Series. R. SAUVAGE (*Compt. rend.*, 1904, 139, 674—676. Compare Auger and Billy, this vol., i, 983).—Phosphorus oxychloride reacts readily at the ordinary temperature with organomagnesium derivatives of the aromatic series to form the corresponding triarylphosphine oxide, R_3PO, and the diarylphosphinic acid, $R_2PO{\cdot}OH$; the following compounds were thus prepared. (1) From magnesium phenyl bromide, *triphenylphosphine oxide*, soluble in alcohol, acetic acid, or benzene, and crystallising from a mixture of benzene and light petroleum in beautiful, white needles melting at 156°. (2) From magnesium benzyl chloride, *dibenzylphosphinic acid*, crystallising from acetic acid in white plates melting at 190—191°, and *tribenzylphosphine oxide*, crystallising from alcohol in needles melting at 217°. (3) From magnesium α-naphthyl bromide, *α-dinaphthylphosphinic acid*, crystallising in plates from acetic acid and melting at 220°, and *trinaphthylphosphine oxide*, not yet obtained in a state of purity owing to its insoluble nature. Phosphorus trichloride reacts with magnesium phenyl bromide with great energy, forming *triphenylphosphine*, which crystallises in large crystals from alcohol and melts at 79°.

M. A. W.